APPLICATION OF PEC NANOPARTICLES TO OIL WELL CEMENTS

A Thesis

by

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ABSTRACT

This thesis focuses on the application of polyelectrolyte complexes (PECs) to oil well cements. Cementing is a critical step in the process of any current drilling and completion program. The hardened cement sheath provides protection and support for the casing string while creating the necessary low permeability barrier to contain underground fluids. Unfortunately, despite advancements in technology and regulation, cement barrier failures still occur and carry with them potentially serious consequences. Leaking fluids lead to irreversible environmental contamination and possible life-threatening blowouts.

Engineers face difficult challenges when designing cement slurries. Competing matters of rheology, fluid loss, gelation, and sedimentation, to name a few, must thoughtfully be considered before formulating the ideal slurry. Polymers are regularly employed to solve these issues but often carry unwanted side-effects. Despite all of the research performed on polymers in oil well cements, little has been done regarding the technology of PECs.

PECs have been highly regarded in the medical industry for their effectiveness in targeted drug delivery systems. They have also made their way to the oil and gas industry for use in hydraulic fracturing and enhanced oil recovery (EOR) processes. The intent of this thesis is to demonstrate that properly designed particles can be utilized in oil well cements to achieve optimum fluid loss control while maintaining acceptable rheology and stability.

The PECs discussed herein were created using polyethyleneimine, carboxymethyl hydroxyethyl cellulose, and polyacrylic acid – common cement additives. They were characterized using high performance liquid chromatography, dynamic light scattering, and total nitrogen analyses. Then, they were added at varying concentrations to cement slurries and studied for fluid loss control, rheology, stability, density, and mixture thickening time. One such combination has demonstrated an excellent fluid loss control of just 38mL/30min. at 40°C even with low concentrations of the primary fluid loss additive. This PEC/slurry mixture has also proven to have ideal rheology and stability as compared to control samples.

DEDICATION

To my beautiful wife, Heidi,

The most important and influential person in my life,

Who selflessly gave of herself to support me while endeavoring to earn my degree.

What a great adventure it has been with you by my side!

ACKNOWLEDGEMENTS

I recognize that a degree cannot be earned in a vacuum. Therefore, I would like to recognize all of the many individuals who have helped me get to where I am.

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I am continually grateful to all of my friends and colleagues at Texas A&M University for their support and encouragement.

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Finally, and most importantly, I would be ungrateful if I failed to acknowledge the enduring and immense support of my parents who have been my biggest fans since the beginning.

CONTRIBUTORS AND FUNDING SOURCES

Contributors

This thesis was supervised by a thesis committee consisting of Professor Jenn-Tai Liang (advisor) and Dr. Ying-Ying Lin of the Harold Vance Department of Petroleum Engineering and Professor Zachary Grasley of the Zachary Department of Civil Engineering.

The PEC nanoparticles, as described in Section 4.2, and the data analyzed in Sections 5.2 and 5.3 were provided by Dr. Ying-Ying Lin of the Harold Vance Department of Petroleum Engineering. All other work for this thesis was completed by student with collaboration from Dr. Ying-Ying Lin.

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NOMENCLATURE

API	American Petroleum Institute
BWOC	By Weight of Cement
CMHEC	Carboxymethyl Hydroxyethyl Cellulose
DLS	Dynamic Light Scattering
EE	Entrapment Efficiency
EOR	Enhanced Oil Recovery
ELSD	Evaporative Light Scattering Detector
FLA	Fluid Loss Additive
GPC	Gel Permeation Chromatography
HPAM	Partially Hydrolyzed Polyacrylamide
HPLC	High Performance Liquid Chromatography
HTHP	High Temperature High Pressure
IOR	Improved Oil Recovery
ISO	International Organization for Standardization
NO	Nitrogen Monoxide / Nitric Oxide
NO_2	Nitrogen Dioxide
PAA	Polyacrylic Acid
PEC	Polyelectrolyte Complex
PEI	Polyethylenimine
PV	Plastic Viscosity

RP	Recommended Practice
SEC	Size Exclusion Chromatography
SGS	Static Gel Strength
SLM	Standard Liters per Minute
TOC	Total Organic Carbon
TN	Total Nitrogen
YP	Yield Point

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

This thesis focuses on the application of polyelectrolyte complexes (PECs) to oil well cements. Cementing is a critical step in the completion process of any current drilling program in order to provide a safe and efficient means of extracting hydrocarbons. The main goal of the cemented sheath is to provide protection and support for the casing string while creating a nearly impermeable barrier to contain underground fluids.

Unfortunately, despite advancements in technology, understanding, and regulation, cement barrier failure is still a regular occurrence that carries potentially serious consequences. Leaking fluids can lead to irreversible environmental contamination and may require significant financial resources to clean up. A sudden influx of unwanted oil or gas can also lead to a serious blowout, which poses risks to both life and property. At a minimum, fluid migration into or out of the wellbore implies a decline in efficiency and a loss of a company's primary product.

1.1 Brief History

One of the earliest recorded, successful applications of cement in an oil well dates back to 1871 when J. R. Hill described the process of pouring cement into a well to seal off a water zone during drilling (Hill, 1871). In the early 1900's the practice of cementing oil wells began to take hold with more and more jobs being performed both in

the United States and around the world (King, 1998; Barnes et al., 2008). As the prevalence of well cementing increased, there quickly arose a need to have a standard set of practices to govern its proper application. This led to the formation of a cementing committee in 1937 by the American Petroleum Institute (API). (Barnes et al., 2008; Calvert et al., 1990). Since then, the industry has made drastic improvements in the process of cementing that has led to safer and more productive wells. Advancements in science have also led to increased understanding of what factors lead to cement failures and how to overcome these issues. Among all of the many challenges engineers face when developing a cement slurry, three of the most important considerations are (1) shortening the transition time during setting, (2) minimizing the fluid loss, and (3) producing a stable slurry with no settling (Rogers et al., 2004). These will be discussed at length below.

1.2 Transition Time and Hydrostatic Head

During drilling, the high pressures encountered underground force fluids such as water, oil, and gas out of the formation, into the wellbore, and upwards toward the surface. This undesired and uncontrolled influx of fluid, known as a "kick," may lead to environmental contamination, significant financial loss or even a life-threatening blowout (Bittleston, et al., 2002; Pelipenko et al., 2004). In order to prevent against such fluid and gas migration, a liquid of high enough density and fluidity (i.e. low viscosity) must be present in the well at all times. This creates the necessary hydrostatic pressure needed to counteract the force of the encroaching formation fluids (King 1998; Bonett et

al., 1996). This pressure, often referred to as hydrostatic head, is created simply by the pressure that the column of fluid exerts on the formation below. For an ideal fluid, excluding friction, and under atmospheric conditions, this is described by the simple equation,

$$p = \rho g Z. \tag{1.1}$$

In this equation 'p' is the hydrostatic pressure imposed by a column of height 'Z' and density 'ρ' with gravity constant, 'g' (modified from Mitchell et al., 2011). Thus, the taller and denser the fluid column, the more pressure it will exert downhole. If this pressure is greater than or equal to the formation pressure, fluid migration into the well is prevented.

During initial cement placement, the slurry is of high enough density and has sufficient fluidity that it provides adequate pressure. Upon standing, however, the cement begins to firm up and forms a highly viscous, rubber-like gel. As this occurs, the yield stress of the slurry increases and, simultaneously, some of the pressure exerted by the column is transmitted laterally to the formation and casing. In combination with the friction in the system, this lower the hydrostatic pressure delivered by the slurry to the bottom of the well. If the gelation is significant enough, the rigid mass will ultimately support its own weight and can even form a bridge in the annulus (Carter et al., 1972). See Figure 1.1.

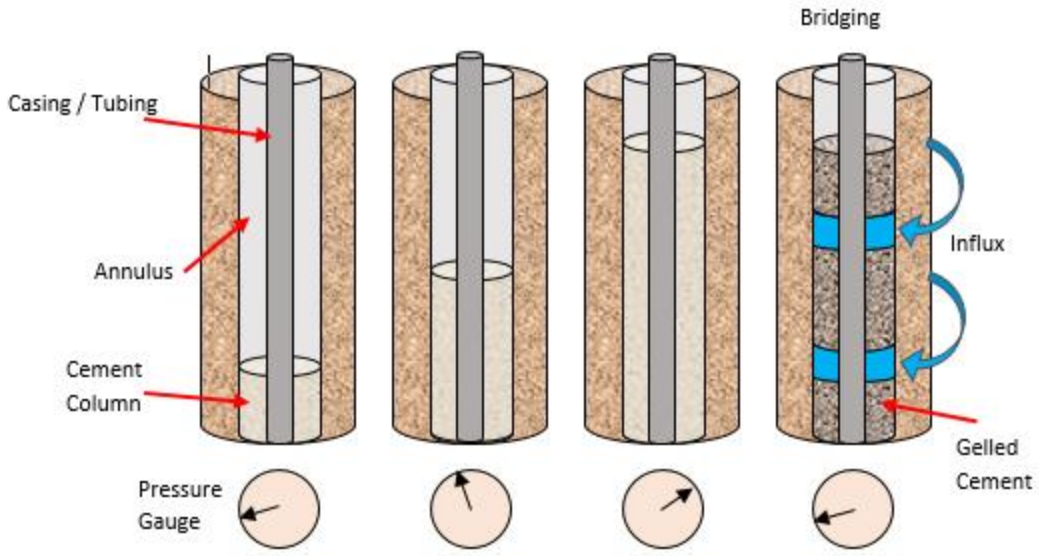


Figure 1.1 Hydrostatic head and cement bridging

When this occurs, the hydrostatic communication is lost, resulting in a significant drop in pressure downhole (Baret, 1988; Bonett et al., 1996; King, 1998). During this stage, the cement is vulnerable to gas and liquid entry into the annulus because the pressure exerted by the formation is now greater than the hydrostatic pressure exerted by the column of cement (Rogers et al., 2004). If not remedied, this will result in the creation of permanent channels in the set cement that will utterly negate its effectiveness as a barrier. For this reason, dispersants are added to the slurry mixture to delay the formation of gel strength and maintain a highly fluid slurry. After this so-called "transition time," the cement will have finally cured enough to oppose the invading fluids and can then finish setting properly.

Loosely state, the transition time of a slurry is defined as the period between low viscosity liquid and high viscosity, nearly impermeable gel or solid. This is shown

schematically in Figure 1.2. In numerical terms, it is often regarded as the period of time where static-gel-strength (SGS) of the slurry is between 100 and 500 lbs/100ft^2 (approximately 5 - 24Pa) (Rogers et al., 2004).

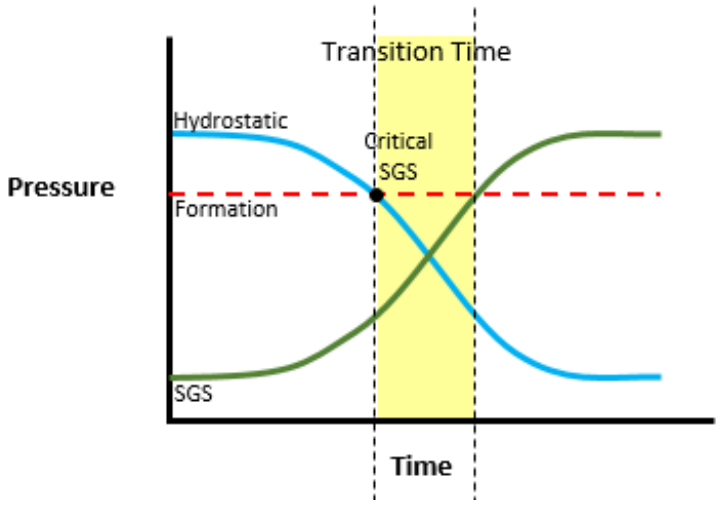


Figure 1.2 Schematic of cement hydrostatic pressure decay and SGS development

Transition time has recently become a point of focus for engineers and scientists because of the susceptibility of cement to fluid entry during this period (Bonett et al., 1996; Rogers et al., 2004). One of the most obvious remedies to this problem is to minimize the time required for the transition to occur by adding accelerators to the slurry (Labibzadeh et al., 2010; Rogers et al., 2004). These additives increase the rate of cement hydration and early strength development. This route is not always feasible, however, as pumping cement into a well is complex and may take more time than is available with an accelerated system. This is especially true in hot wells where the temperature already greatly accelerates the curing rate.

Alternatively, delaying the loss of hydrostatic pressure can be achieved through chemical means, such as the use of a friction reducing agent, or through mechanical means, such as through cement pulsation or casing vibration (Newman et al., 2001; Cooke et al., 1988). These mechanisms work by keeping the cement in a fluid state until a certain degree of cement hydration is achieved. After the cement has cured sufficiently, the cement will have generated enough strength to prevent fluid migration and the subject of hydrostatic head is no longer an issue (Bonett et al., 1996).

1.3 Fluid Loss Control

In most oil and gas wells, the underground rock surface is highly permeable to fluid and gas flow; this is what makes them ideal for hydrocarbon extraction. When cementing, however, this permeability can be detrimental to the job's success. As the cement is forced under high pressures into the annular space, the rock face filters out the fluids and leaves behind only the solid cement components. This fluid loss has several important implications on the placement and quality of the cement sheath. Some of these issues include:

1. Reduced slurry volume leading to incomplete coverage of cement over the desired zone (Bannister et al., 1985; Rogers et al., 2004).
2. Slurry shrinkage causing gaps to form between the cement-formation interface or the cement-casing interface (also known as a micro-annulus) (Dusseault et al., 2000).

3. Incomplete hydration of the molecules that inhibits proper setting of the cement and increases its permeability (Zhang et al., 2010; King, 1998; Bülichen et al, 2012).
4. Decay of the hydrostatic head resulting in insufficient pressure to hold back the invading formation fluids (as previously mentioned) (Carter et al., 1972; Bannister et al., 1985).
5. Increasing slurry viscosity that persists until either it is not pumpable or until the pressure needed for pumping exceeds the formation breakdown pressure resulting in an undesired fracture (King, 1998; Bülichen et al, 2012).

All of these issues can ultimately result in unwanted fluid communication in the wellbore and may lead to leaks and barrier failures. For these reasons, controlling fluid loss is of the utmost concern.

In order to ensure the integrity of the cement, fluid loss additives (FLA) are typically added to the slurry mixture. FLAs promote the development of a low permeability filter cake between the cement slurry and the formation. Several mechanisms have been proposed to explain how this occurs. In general, polymeric FLAs are believed to function by either decreasing the permeability of the filter cake or increasing the local interstitial filtrate viscosity (Bülichen et al, 2012; Desbrieres, March 1993; Desbrieres November 1993).

Of the two mechanisms, Desbrieres demonstrated that a decreased filter cake permeability is the major contributing factor to the overall fluid loss control. Desbrieres expands on this idea by proposing three explanations for the decreased permeability: (1)

decreased pore size, (2) sedimentation, and (3) pore plugging. With regard to pore size, polymers may cross-link or entangle with themselves or other particles in the aggregate to create large macromolecular chains. These polymeric matrices create low permeability films between the cement and the formation. These molecules may also physically adsorb to pores in the filter cake, thereby reducing the effective size of the opening.

Sedimentation occurs when additives are used that alter the interactions between cement particles. This allows them to arrange in a more concise manner and pack tighter so as to inhibit fluid flow. It is important to note that sedimentation as a form of fluid loss control is really only applicable to laboratory static filtration tests. As is discussed below, a slurry that demonstrates sedimentation, although helpful for fluid loss control in the lab, is not acceptable for field applications.

Finally, pore plugging is achieved by particles that physically protrude into the pores of the filter cake and seal off the openings (Bülichen, 2012; Desbrieres, March 1993; Desbrieres November 1993). For instance, cellulosic compounds swell in the presence of water and expand to fill the empty spaces in the pores. As an added benefit, the bound water is held tightly in place so it is prevented from filtering out into the formation (Plank et al., 2009).

The API has stipulated that no more than 100mL of fluid can be lost by a cement slurry, during static filtration tests, to be acceptable for field applications (API RP 10B-2). In contrast, Bannister and Lawson argue that this is too high considering fluid loss continues long after cement has been initially placed in the well (Bannister et al., 1985).

Instead, they proposed that by keeping the standard fluid loss to a minimum, less than about 10-30mL in 30 minutes, the risk of fluid and gas channeling could be greatly reduced. This sentiment is further supported by Devereux who suggests keeping fluid loss to around 50mL/30min to prevent fluid channeling or 15mL/30min to prevent gas migration (Devereux, 1998).

1.4 Slurry Stability and Sedimentation

Sedimentation occurs when the cement particles in a slurry begin to settle leading to the development of "free fluid" at the top of a cement column. This can be divided into two types, hindered settling and differential settling, as described by Greaves and Hibbert (Greaves et al., 1990). They explain that hindered settling occurs in fairly concentrated suspensions where the cement particles flocculate and form a single cohesive unit. According to this theory, all particles settle at the same rate and therefore maintain their relative positions to one another. This leads to the development of clear fluid at the top of a cement column that is easily identifiable.

In differential settling, however, Greaves and Hibbert explain that particles will settle at different rates according to Stoke's Law,

$$V = \frac{2(\rho_p - \rho_f)gr^2}{9\mu}, \tag{1.2}$$

where 'V' is the settling velocity, 'ρ_p' and 'ρ_f' are the densities of the particle and fluid respectively, 'g' is the acceleration due to gravity and 'r' is the radius of the particle.

Differential settling often occurs in dilute mixtures or in slurries containing too many friction reducers because the cement particles are unable to cohere to one another.

A form of free fluid may also be present in this case, but is usually not noted because the color and transparency is closer to that of the remaining slurry than that of water. This is a result of the small particles staying suspended near the top of the cement column while the larger particles settle to the bottom. These fine cement grains will not set properly and should therefore be considered part of the free fluid (Greaves et al., 1990).

In either case, the development of free fluid is an indication of an unstable slurry and is therefore not appropriate for use in an oil well. The API has stipulated that, in laboratory testing, "the free fluid for [class H] well cements shall not exceed 5.9%" (API Specification 10A, 2010). Although this may be considered acceptable according to the standard, any amount of free water may result in a loss of compressive strength in parts of the column (Roshan et al., 2010) and may lead to gas migration due to inconsistent coverage along the wellbore (Bonett et al., 1996). In deviated or horizontal wells, sedimentation is especially harmful because the free water will migrate to the high side of the well leaving large portions of the casing un-cemented (King, 1998) (See Figure 1.3).

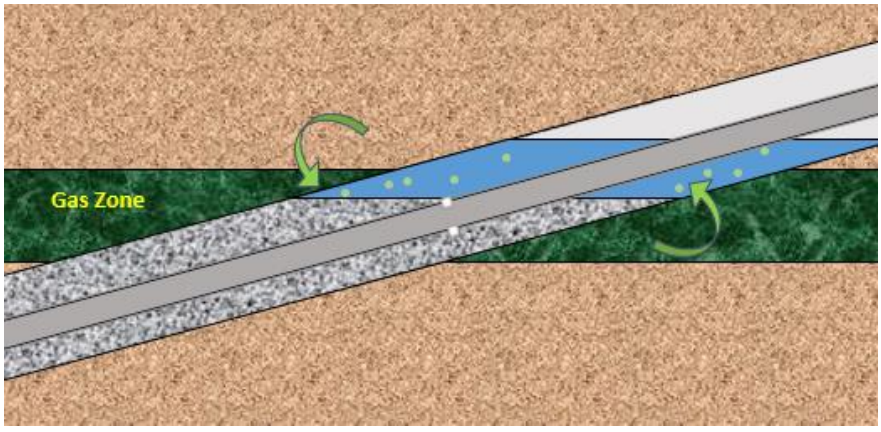


Figure 1.3 Free water in deviated wells

To prevent sedimentation, additives are often employed to suspend particles in the mixture. These additives promote the formation of gel-strength by enhancing the attractive forces between the cement grains. If the gel-strength development is significant enough, both types of sedimentation can be avoided. However, these types of materials, by their nature, tend to increase the viscosity of the slurry (Parks et al, 1986). In fact, as noted from Equation (1.2), an increase in viscosity is beneficial as it leads to a decrease in settling viscosity. If the slurry becomes too viscous, however, it becomes unpumpable. On the other hand, if the slurry is not viscous enough, or if sufficient gel-strength does not develop, sedimentation will occur as previously discussed. The optimal slurry is found somewhere in between these two extremes. It has been recommended that the slurry yield stress be between 7 and 25 Pa during lab testing to be considered suitable for most oil well cementing applications (Baret et al., 2002).

1.5 Polymer Use in Oil Well Cements

Based on this knowledge of transition time, fluid loss, and sedimentation, one can see the difficult challenges associated with designing a cement slurry. The ideal slurry must have low viscosity and low yield stress during mixing and pumping. This ensures sufficient hydrostatic head, ease of placement, and adequate displacement of drilling mud (King, 1998). Once in place, the slurry must then be able to resist settling by developing sufficient gel strength to suspend particles. However, the gelation must not be so substantial before setting as to cause bridging or a significant decay of hydrostatic pressure. Finally, the transition time from low viscosity, low yield stress

liquid to nearly impermeable, rigid mass must be short. All of this must be accomplished without a significant amount of water loss from the slurry. Although this seems like a daunting task, the proper application of polymers can individually remedy nearly all of these issues.

Polymers have been widely used in the oil and gas industry for many years and have seemingly limitless applications. In drilling fluids, polymers have been used as friction reducers, viscosity modifiers, and fluid loss control agents (FLAs) (Mitchell et al., 2011; Lucas et al., 2009). In hydraulic fracturing, various types of polymers are utilized for creating fractures and carrying proppant to the newly formed channels to keep them open (Montgomery, 2013). In cementing, polymers are often used to alter the rheological characteristics of the slurry, modify the setting time, prevent fluid loss or even improve the compressive strength of the set cement (Mitchell, R.F. et al., 2011; Abbas et al., 2014). Polymers have even found a niche in well logging where polymer based nanoparticles can be used as sensors to locate oil and aid in transmitting electrical signals through hydrocarbons to equipment at the surface (Advincula, 2014). Other applications include emulsifying or demulsifying solutions, preventing scaling, creating anti-corrosion coatings, and improving oil production through enhanced oil recovery (EOR) methods (Lucas et al., 2009; Advincula, 2014).

Among the common polymers found in this industry are polyethylenimine (PEI), derivatives of cellulose including carboxymethyl hydroxyethyl cellulose (CMHEC), and polyacrylamides including polyacrylic acid (PAA).

1.5.1 Polyethylenimine

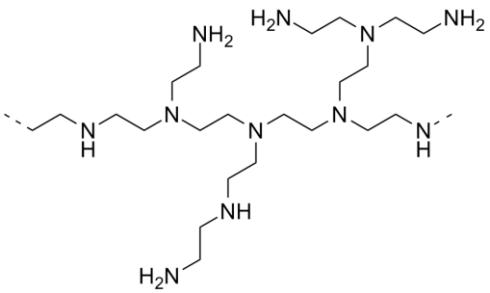


Figure 1.4 Polyethyleneimine (Polyethylenimine 2016)

Polyethylenimine (Figure 1.4), abbreviated PEI, is a very versatile polymer that has found numerous industrial applications. Some of its functions include acting as a transfection agent in cellular biology (Boussif et al., 1995), capturing and storing carbon dioxide (Xu et al., 2002), and enhancing the wet strength of paper (Wagberg, 2001).

In the oil and gas cementing business, high molecular weight PEI has often been used as a FLA because of its exceptional ability to control fluid loss when mixed with sulfonated polymers that are common dispersants and retarders (McKenzie, 1984). The mechanism behind the fluid loss control of PEI and sulfonated material was described by Plank et al. (2009) and Dugonjić-Bilić et al. (2011). They proposed that the two molecules create a polyelectrolyte complex (PEC) that effectively seals off the permeable channels of the filter cake (Plank et al., 2009; Dugonjić-Bilić, 2011). PEI's ability to form complexes of this sort is due to its poly-electrolytic properties. At low pH values, the amine functional groups become protonated and the molecule becomes poly-cationic. In this condition, ionic interactions cause PEI to quickly form polymer complexes with poly-anionic molecules.

Despite its advantage as a FLA, PEI is also known to cause several issues when added to cement. First, when PEI is combined with sulfonated materials, the mixture is prone to settling and developing free water (Desbrieres 1993, March; Desbrieres 1993, November). According to Desbrieres, this sedimentation may actually account for the added fluid loss control benefits of this system. Second, when PEI is used alone, it causes a significant increase in slurry viscosity while only marginally improving fluid loss control. At concentrations large enough to provide adequate control, typically above 3%bwoc, the slurry becomes excessively viscous and even unpumpable (Plank et al., 2009). Although the issues of increased viscosity and sedimentation can be partially overcome by altering the concentrations of PEI and sulfonated compound (Plank et al., 2009), the solution often requires higher concentrations of PEI that is not always cost effective.

1.5.2 Carboxymethyl Hydroxyethyl Cellulose

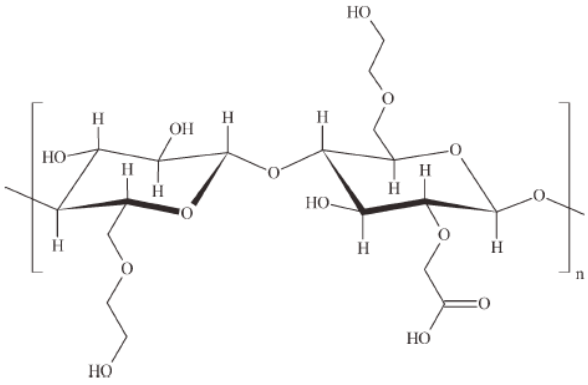


Figure 1.5 Carboxymethyl hydroxyethyl cellulose (Bülichen, D. and Plank, J., 2012)

Carboxymethyl Hydroxyethyl Cellulose (Figure 1.5), abbreviated CMHEC, is one of several derivatives of cellulose that are commonly used in the oil and gas industry. CMHEC has been used as an additive in cements since the 1950's mainly because of its effectiveness at preventing fluid loss and its ability to retard cement at temperatures below 250°F (120°C) (Nelson, 1990; Greminger, 1958). Unlike other cellulose derivatives that degrade quickly as the temperature increases, CMHEC is known to be thermally stable at higher temperatures (Tylose® HC 50 NP2 Specifications, 2017). It is also known to be resistant to both bacterial attack and degradation from acids and salts over a broad range of concentrations (Greminger, 1958; Tylose® HC 50 NP2 Specifications, 2017). The mechanism behind CMHEC as a FLA has been shown to be dependent upon its concentration in the slurry. At low concentrations the molecule adsorbs to the cement particles in the filter cake to reduce permeability. At high concentrations, above the threshold or overlapping concentration, the molecules entangle and form associated polymer networks that obstruct the pores in the filter cake (Bülichen et al., 2012). CMHEC is also effective at preventing fluid loss by binding large amounts of water. This bound water is no longer free to move about in the mixture and therefore cannot be filtered out into the surrounding formation (Plank et al., 2009).

A side effect of using nearly any cellulosic derivative is its inherent tendency to increase the slurry viscosity when used in an aqueous solution. Although cellulose compounds can be beneficial in preventing sedimentation (Roshan et al., 2010), the significant increase in thickness often makes the slurry difficult to manage (Nelson,

1990). Perhaps somewhat contradictory to logic, this effect is even further exacerbated by the use of certain incompatible viscosity reducers that are commonplace in the industry (Crema et al., 1989).

The viscosity of CMHEC can be adjusted through the addition of certain crosslinking agents. For example, Podlas (1977) showed that chromium and aluminum have the ability to increase the viscosity of a CMHEC solution by linking the polymers together (Podlas, 1977). The degree of substitution of the hydroxyethyl and carboxymethyl groups will also affect the physical properties of the polymer including retarding effects, temperature stability, and compatibility with salt solutions (Nelson, 1990; Podlas, 1977; Tylose® HC 50 NP2 Specifications, 2017).

Temperature is also a concern for any cellulose derivative. With increasing temperature, these additives show a decrease in effectiveness against fluid loss. Although more additive may provide a degree of improvement against the effects of temperature, care must be taken to prevent over retardation of the slurry (Nelson, 1990).

1.5.3 Polyacrylic Acid

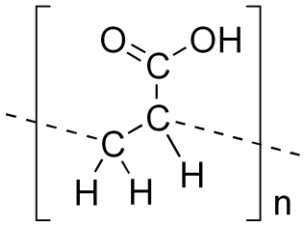


Figure 1.6 Polyacrylic acid (Polyacrylic acid 2016)

Polyacrylic acid (Figure 1.6), abbreviated PAA, has served a myriad of functions in the field of hydrocarbon extraction. Some of its most common and widely used

applications are in water cleanup (Amjad, 1996) and scale inhibition (Fink 2015). In hydraulic fracturing, PAA may also be used as a friction reducer and a component in "slick water" to improve pumpability during a treatment (Montgomery, 2013).

PAA has also been known for many years to be beneficial in oil well cementing. As a co-polymer with acrylamide, PAA is a very effective FLA over a wide range of temperatures, as shown by McKenzie and McElfresh (McKenzie et al., 1982). At especially high temperatures, the hydrolysis of acrylamide to acrylic acid provides an additional measure of retardation that makes this combination useful in hot wells (Crema et al., 1989). Its effectiveness of as a retarder is likely due to its poly-anionic nature. The negative charge is thought to reversibly complex with the positively charged particles in the slurry thereby temporarily blocking nucleation sites and inhibiting the hydration of cement (McKenzie et al., 1982).

Another benefit of PAA is its usefulness as a friction reducer in cement slurries (Lea, 1952). By binding to positively charged molecules, PAA changes their zeta potential to zero or even negative. This creates repulsive forces between cement grains and prevents electrostatic attractions (Ferrari et al., 2010). An even higher level of friction reduction can even be achieved by grafting hydrophilic polyether side chains to the primary hydrocarbon backbone (Fiat et al., 2012). These long side chains add an additional level of repulsion by creating steric stabilization of the molecules to prevent flocculation.

1.6 Polyelectrolyte Complex

Polyelectrolyte complex (PEC) formation has become an innovative and rapidly growing area of research in recent years (Lankalapalli et al., 2009). PECs are easily formed by the self-assembly of highly ionic polymers dissolved in a polar solvent (Gubbala, 2012). The stability of the complex can be modified to suite individual applications by manipulating variables such as temperature, pH, salinity, molecular weight, and component ratios in solution (Gubbala, 2012). PEC systems can even be designed to withstand extreme environments, such as high temperature and acidity, but then decay rapidly under predetermined conditions. These properties make PECs ideal for use in targeted drug delivery research for medical applications (Lankalapalli et al., 2009). For example, a drug delivery system targeted for the colon has been created that releases medication in response to an increase in pH (Win et al., 2003). This allows the complex to pass through the acidic environment of the stomach without releasing the drug, where it would otherwise decay or cause undesirable reactions. Once it reaches the colon, the complex breaks causing the drug to release where it can provide the most benefit to the patient with the fewest side effects.

PECs have found some novel applications in the oil industry as well. For instance, Barati et al. (2012) demonstrated that gel-breaking enzymes could be effectively entrapped in PEC nanoparticles that would then release after a predetermined amount of time (Barati et al., 2012; see also Barati et al., 2011). This delayed release allowed the enzymes to be added to guar based hydraulic fracturing fluid without breaking the gel structure until such time as was necessary. The PEC also serves to

protect the sensitive enzymes from the harsh underground environments found in most oil and gas wells. In another example, Cordova et al. (2008) used a PEC to entrap a cross-linking agent to delay gelation of partially hydrolyzed polyacrylamide (HPAM) (Cordova et al., 2008). The purpose of this was to allow the gelant to be pumped deeper into water injection wells before the gelation occurred. This helped improve the sweep efficiency of water injection by plugging highly permeable channels deep in the reservoir.

In the aforementioned examples, it is observed that the viscosity of the mixture is effectively controlled by the PEC nanoparticle system. This ability to manipulate mixture viscosity by entrapping the components in a nanoparticle has potentially beneficial applications to cementing operations where rheology plays a significant role.

An added benefit of utilizing PEC systems in oil well applications is the ease with which such a system could theoretically be scaled up to meet real world applications. Production of PEC nanoparticles can often be accomplished with basic mixing procedures without the need of complicated protocols often required of other chemically engineered polymers. This ultimately saves time and cost making this technology easier to deploy in the field with minimal training of personnel (Lin, Y. Y., personal communication, September 2016).

CHAPTER II

PROBLEM STATEMENT AND STATEMENT OF PURPOSE

2.1 Problem Statement

Recent data has shown that hydrocarbon leakage from wells is a continual problem. An estimated 3.4% of wells drilled between 2008 and 2013 showed signs of leakage caused by casing and cementing barrier failures (Jackson, 2014; Vidic et al., 2013). Although this data was taken from a limited dataset, similar or worse results have been observed for various other locations around the US and around the world (Davies et al., 2014). Improved understanding, increased regulation, and heightened awareness have surely led to the marked decrease in well failures, but in a field where leaks of this sort are strictly unacceptable, this still remains a significant problem. Data also point to the fact that unconventional gas wells are approximately six times more likely to leak than conventional oil wells (Jackson, 2014). As extraction of these unconventional resources becomes more prolific, this problem will only worsen unless corrective actions are taken.

Polymers have been used in oil well cements for many years to control the undesired influx of fluids. Most polymers, however, cause one or more undesired side effects. As previously discussed, the formation of a cement slurry requires, among other considerations, the interplay of various rheological properties. An additive that is useful in lowering slurry viscosity for pumping often inadvertently leads to an unstable slurry that is prone to sedimentation. Alternatively, an additive that is formulated to promote

gel strength to reduce settling is prone to bridging and simultaneously increases the viscosity of the fluid. What is left somewhat incomplete is the development of a system that can provide good fluid loss control, inhibit gas migration, and prevent sedimentation while avoiding the unwanted side effects.

Although the applications of PECs in medicine, cosmetics, and even parts of the oil and gas industry have been known for some time, very little work has been done to exploit this technology for oil well cementing. The closest resemblance of the application of PECs in cementing was discussed by Plank et al. (2009) and Dugonjić-Bilić et al. (2011) who proposed the formation of a polymer complex as a mechanism behind the improved fluid loss control of a slurry. In these works, however, the authors simply sought to understand the mechanism behind a fluid loss control system that was already in use but did not mention the possibility of manipulating the complex to achieve a targeted application. More recently, Chatterji et al. (2014) discussed the encapsulation of FLAs using materials such as waxes to control fluid loss and viscosity over time. In this work, however, no consideration was given to utilizing the technology of PECs, with their potential functionality, as a means of achieving this goal (Chatterji et al., 2014). Just as PEC have been used in medicine to realize a specific goal without the unwanted side effects, it is proposed that a properly designed PEC system can enhance the effects of polymers used in cementing without the negative interactions.

2.2 Statement of Purpose

With all of these considerations in mind, the main goals of this thesis are:

1. To provide evidence that new PEC systems, comprised of common oilfield polymers, can be developed to provide effective fluid loss control.
2. To demonstrate that said nanoparticles can produce slurries with ideal physical properties (rheology, density, stability, thickening time, etc.) meeting API standards where applicable.
3. To further demonstrate the system's ability to entrap a FLA with the goal of reducing or delaying the viscosity increase of a slurry.

Although the scope of this thesis is limited to a proof of concept view of the application of PECs in cementing, consideration is also given to the ultimate end goal of developing a system that is cost-effective, efficient, and easy to deploy in the field.

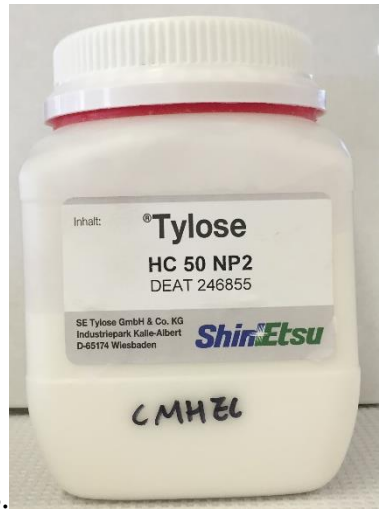
CHAPTER III

RAW MATERIALS

The main raw materials and reagents used for this study are cement and polymers of PEI, CMHEC, and PAA, (Figure 3.1, A, B and C respectively).

- The cement was a general purpose Portland cement of classification H provided by Lafarge (Lafarge North America Inc. of LafargeHolcim group, Chicaco, IL).
- The PEI polymer was provided by Polysciences (Polysciences Inc., Warrington, PA) with a nominal molecular weight of 2,000kD. The purchased solution was approximately 25% by weight PEI.
- CMHEC reagent, under the product name HC 50 NP2, was provided in dry powder form from SE Tylose (SE Tylose GmbH & Co KG, Wisebaden, Germany). This low molecular weight/low viscosity polymer was developed specifically for oil well cementing applications.
- PAA was supplied as an approximately 42% by weight solution by SNF Inc. under the name Flosperse™ 3000 (SNF Holding Co., Riceboro, GA).

A. 

B. 

C. 

Figure 3.1 Raw materials used in this study. A) PEI, B) CMHEC, C) PAA

For comparative purposes, a commercially available FLA and a corresponding retarder were also used, both provided by Halliburton (Halliburton, Houston, TX). See Figure 3.2 A and B respectively. The FLA, Halad®-9, is a blend of cellulose based material and dispersants in dry form. It is intended for use in wells with temperatures up to 300°C. The retarder, as recommended by the manufacturer, was HR®-5, a chemically modified lignosulfonated material.

A. 
B. 

Figure 3.2 Commercially available cement additives from Halliburton. A) Halad®-9 FLA; B) HR®-5 Retarder

CHAPTER IV

EQUIPMENT AND PROCEDURES

4.1 General Testing Information

The following general information is useful for understanding procedures followed in this thesis.

- All tests were performed following appropriate laboratory procedures, standard testing practices, and API specifications, where applicable. It is worthwhile to note that other characteristics, such as compressive strength and SGS, are also important but were not tested here due to a lack of instrument availability. Regardless, the current approach is appropriate since the main focus of this thesis is simply a proof-of-concept of the application of PECs to cementing.
- Since CMHEC itself acts the primary fluid loss control agent in this study, tests were designed around its concentrations in solution. In other words, the amount of PEC in the slurry is dependent upon the concentration of CMHEC desired. The purpose of this was to make it easier to compare results of CMHEC when added as a raw material vs. CMHEC added as part of a polymer complex.
- All percentages stated in this document are given on a "by weight of cement" (bwoc) basis, unless otherwise stated.

- When aqueous solutions of PECs were used, a correction for the water's mass had to be taken into account so that the total water in the final slurry was always maintained at the required 38%. This placed a limit on the amount of PEC that could be added to a cement mixture before the water weight was exceeded. This limit corresponds to slightly more than 0.35% CMHEC as a PEC, indicating a potential downside of this system.
- The EE is defined as the mass percentage of a compound that is entrapped in a PEC as compared to the total mass of that compound in the mixture. In equation form, this can be written as,

$$\% \, EE = \frac{Entrapped \; Analyte}{Total \; Analyte} x100 \tag{4.1}$$

or alternatively,

$$\%EE = \frac{Total \; Analyte - Free \; Analyte}{Total \; Analyte} x100 \tag{4.2}$$

4.2 Polyelectrolyte Complex Preparation and Characterization

The PEC nanoparticles for this study were provided by Dr. Y.Y. Lin who is experienced in the preparation and optimization of such systems. Nanoparticle preparation was achieved by first creating stock solutions of the individual components in water: 6% PEI, 3% PAA, and 2% CMHEC by weight. Then, the appropriate amount of PAA stock solution was added continuously to the PEI solution while mixing in a high speed blender. Finally, the CMHEC solution was added to the PEI/PAA mixture,

with continued mixing, to produce the final PEC. The mixture ratios and component loading concentrations for the nanoparticle formulation are given in Table 4.1.

Component	Ratio (parts)	% by weight	Concentration (ppm)
PEI	3	1.6364	16,364
PAA	3	0.8182	8,182
CMHEC	5	0.9091	9,091

Table 4.1 Composition of PEC nanoparticle

The PEC nanoparticles in this thesis were then characterized using (1) high performance liquid chromatography for determining the EE of CMHEC, (2) total nitrogen analysis for quantifying the EE of PEI, and (3) dynamic light scattering for the measurement of particle size and zeta potential.

4.2.1 High Performance Liquid Chromatography

4.2.1.1 Background

High performance liquid chromatography (HPLC) is a common technique used to separate and quantitate different compounds in a mixture. In general, the instrument works following the general theory of chromatography consisting of a mobile phase (or eluent), a stationary phase, and a detector. The mobile phase is responsible for carrying the sample and its constituents along the stationary phase where molecules are segregated for detection. Some molecules have a higher affinity for the stationary phase than others causing them to spend different amounts of time in the system. This is

responsible for the separation. For example, a polar molecule will tend to be more attracted to a polar stationary phase than a non-polar molecule. Therefore, the non-polar molecule will be pushed through the system quickly. Meanwhile, the polar molecule will be hindered from passing through the system resulting in slow elution. In schematic form, this is demonstrated in Figure 4.1.

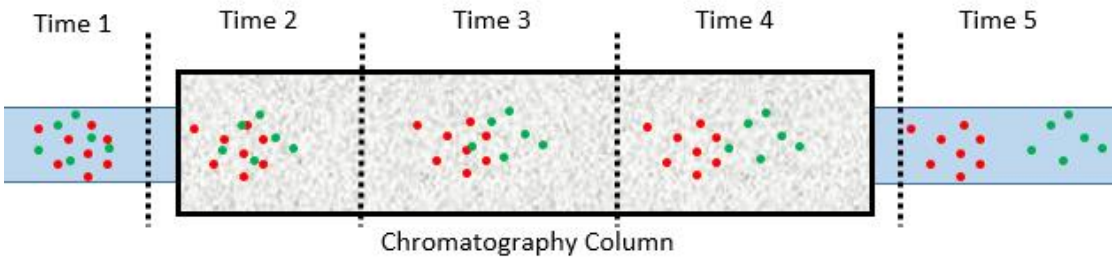


Figure 4.1 Diagram of chromatographic separation. Red dots represent molecules of high affinity to column (stationary phase). Green dots represent molecules of lower affinity to column. Each time segment represents a "snapshot" of the molecules and their relative location at a given time

In a similar manner, characteristics such as size, charge, hydrophobicity, hydrophilicity, or viscosity can be utilized with an appropriate stationary phase to achieve separation. Once segregated, the isolated compounds can then be analyzed individually.

In this HPLC analysis, the mobile phase was an aqueous mixture of water and ammonium acetate. The stationary phase was a unique type of permeable gel with varying pore sizes packed tightly into a cylindrical column. This gel permeation chromatography (GPC), as it is known, is a type of size exclusion chromatography (SEC) that separates compounds by their molecular weights. Larger particles are excluded from entering the smaller openings in the gel and therefore pass through the

media quicker than the small particles that spend more time caught up in pores. After separation in the column, the particles pass through an evaporative light scattering detector (ELSD) for quantitation. Figure 4.2 gives a diagram of the fluid's flow through the HPLC system.

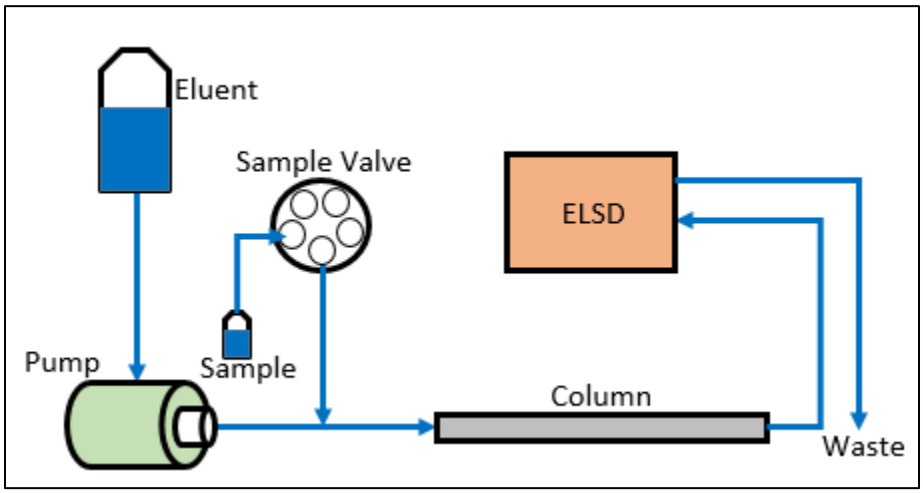


Figure 4.2 Basic fluid flow diagram of HPLC

ELSD is a destructive type of detection that takes advantage of volatility differences to remove analytes from the mobile phase solution. As the analyte-containing eluent flows into the detector, a nebulizer first transforms the solution from a continuous liquid into a fine mist. This mist then passes into an evaporation tube where highly volatile substances, such as the mobile phase, are evaporated off leaving behind only the non-volatile compounds of interest. The dry analyte then passes through an optical chamber where a laser shines a beam of monochromatic light onto the incoming particles. The particles cause the light to scatter onto a photodiode set at a fixed angle with respect to the incident path. The electromagnetic radiation is then converted to an electrical voltage relative in size to the intensity of deflected light. This voltage is read

by the software and is plotted vs time on a graph. By comparing the relative peak area of a sample's voltage spike to that of a standard, the analyte's concentration can be determined. Figure 4.3 provides a schematic of flow through the ELSD.

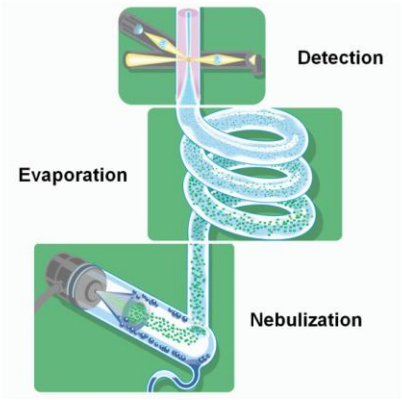


Figure 4.3 Schematic of analyte detection by ELSD (Agilent 1260 Infinity ELSD User Manual, May 2012)

Three scattering regimes are known to occur in ELS detection based on the particle's relative size to that of the wavelength of incident light: Raleigh, Mie, and refraction-reflection (Figure 4.4) (Water's Evaporative Light Scattering Detector Operator's Guide, 2006-2009).

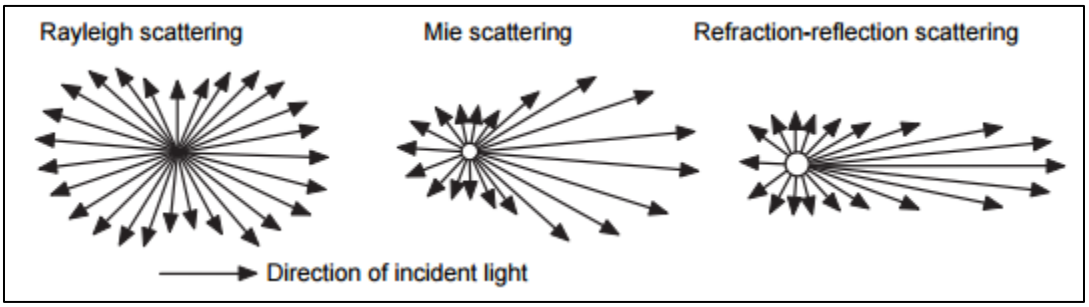


Figure 4.4 Light scattering regimes (Water's Evaporative Light Scattering Detector Operator's Guide, 2006-2009)

In a practical sense, what is measured by the detector is related to the total mass of material in the optical pathway rather than individual particles. Furthermore, higher concentrated samples will deflect more light and produce a higher response. Therefore, during the elution of a single compound, the detector may enter multiple scattering regimes. This fact results in a response from the ELSD that is not linear over a large range of concentrations (Water's Evaporative Light Scattering Detector Operator's Guide, 2006-2009). Consequently, a power law curve of the form $y = bx^a$ is used as it often provides a good fit for the calibration data. Symbols 'a' and 'b' are fitting parameters required to match the curve to the data.

In this investigation, an Agilent 1260 Infinity HPLC with ELSD (shown in Figure 4.5) was used for quantitation of CMHEC (Agilent Technologies, Santa Clara, CA).

Figure 4.5 Agilent 1260 Infinity HPLC with ELSD

The GPC column used for separation was Waters Ultrahydrogel 250 (Waters Corporation, Milford, MA). This column was chosen because of its selectivity for polymers ranging from 1,000 to 80,000 Daltons. This is the range required to separate PAA (approximately 14kd) and CMHEC (approximately 80kd).

Several problems may arise from using such a system, however. One issue is the potential for peak interference with CMHEC because its molecular weight is at the high end of the column's capability. Theoretically, all compounds larger than the column's range, such as PECs and PEI, will elute at the same time. To ensure there is no interference with CMHEC, PEC nanoparticles must first be removed prior to injection. For PEI, however, there does not appear to be an issue with interference. It is interesting to note that PEI actually elutes after CMHEC despite its larger molecular weight (see Figure 5.2 below). More discussion on this is given in Chapter 5 below.

It is also important to mention that the polymers used in this investigation may have broad molecular weight distributions. This could potentially result in a single compound producing multiple peaks in a chromatogram, or at very least, one broad peak. If, however, the standard is considered to be homogenous and well dispersed, a single peak in a chromatogram may be used as a reference for the amount of analyte in the sample.

This method also assumes that PECs entrap all molecules of a given polymer equally well despite some differences in molecular weight. In other words, it is assumed the larger molecules of CMHEC are taken up in equal amounts as the smaller molecules. If this were not the case, the chromatographic analyses of CMHEC could be misleading.

Despite the possible shortcomings and issues, it must be kept in mind that this test is only meant to provide a reasonable estimate of the amount of CMHEC in a sample. Therefore, there is no need to perform a rigorous validation of the procedure. Regardless, basic considerations such as interference, peak resolution, correlation coefficient and peak shape will necessarily be considered to ensure accuracy. Furthermore, all samples will be injected in duplicate to create further confidence in the results.

4.2.1.2 System Parameters and Sample Preparation

Table 4.2 provides a summary of the important parameters used to test the samples on the HPLC system.

Instrument	Parameter	Value	Unit
ELSD Agilent 1260 Infinity	Nebulizer Temp	40.0	°C
	Evaporator Temp	60.0	°C
	Gas Flow Rate	1.60	SLM
HPLC Agilent 1260 Infinity	Flow Rate	0.75	mL/min
	Column Temp	35.0	°C
	Injection Volume	75	µL
	Mobile Phase	50:50	Buffer : Water
	Buffer (Ammonium Acetate)	0.1	M
	Buffer pH	9.5	-
Column	Waters Ultrahydrogel 250, 6µm, 7.8mm x 300mm		

Table 4.2 HPLC system parameters

The current analyte in question, CMHEC, acts as the primary FLA in the cement system. Although the total amount of CMHEC added to the system is known, the

amount of entrapped analyte is not easily measured by direct means. Therefore, to determine the EE of the system, it was necessary to measure the free CMHEC or, in other words, the CMHEC not entrapped in a complex. To accomplish this, the nanoparticles were first removed from the solution. This was done by centrifuging an aliquot of sample for 20-30 minutes at 14,800 rpm. Immediately following centrifugation, approximately 2 to 2.5g of sample was accurately weighed into a 100mL volumetric flask followed by 15 drops of ammonium hydroxide (NH_4OH). By making the solution alkaline, the sidechains on the PEI molecule are neutralized. This inhibits its ability to create new PECs from the free components left in mixture. The solution was then diluted to 100mL with deionized water and shaken to mix. The prepared sample was then filtered through a 0.45μm syringe filter into a vial and placed on the HPLC for analysis.

The standards were prepared by creating alkaline solutions of 25, 50, 100, 150, 200, and 250ppm CMHEC in deionized water. These solutions were all filtered using 0.45μm syringe filters to remove contaminants. See Table 4.3 for a summary of standard preparation procedure.

Name	Conc.	Units	Preparation
Stock CMHEC STD	0.50	% (m/m)*	0.5g CMHEC powder diluted to 100g with H_2O
Working STD 1	25	ppm	0.5g Stock + 15drops NH_4OH diluted to 100mL with H_2O
Working STD 2	50	ppm	1.0g Stock + 15drops NH_4OH diluted to 100mL with H_2O
Working STD 3	100	ppm	2.0g Stock + 15drops NH_4OH diluted to 100mL with H_2O
Working STD 4	150	ppm	3.0g Stock + 15drops NH_4OH diluted to 100mL with H_2O
Working STD 5	200	ppm	4.0g Stock + 15drops NH_4OH diluted to 100mL with H_2O
Working STD 6	250	ppm	5.0g Stock + 15drops NH_4OH diluted to 100mL with H_2O

*%(m/m) = percent by mass

Table 4.3 HPLC standard preparation

4.2.1.3 Calculations

A calibration curve was created using Agilent's ChemStation software to fit a power law curve to the measured standards. The curve is of the form

$$y = Bx^A \tag{4.3}$$

For this application, y is the measured peak area in area counts, x is the standard's concentration in ppm (ng/mL), and B and A are values determined by curve fitting. Making substitutions for x and y with their representative names and rearranging Equation (4.3) gives Equation (4.4), the concentration of CMHEC (in ppm) in the injected sample.

$$[CMHEC]_{inj} = 10^{\frac{Log\left(\frac{Peak\ Area}{B}\right)}{A}} \tag{4.4}$$

To calculate the concentration of CMHEC in the original sample, percent dilution must be taken into account. For example 2.5g of sample diluted to 100mL with water is equivalent to 2.5% (mass/volume) or a factor of 0.025. This assumes a solution density of 1g/mL; a very reasonable assumption for the dilute aqueous polymer solutions

used in this investigation. With these additions, the concentration of CMHEC in the original sample becomes,

$$[CMHEC]_{sample} = [CMHEC]_{inj} \frac{dilution(mL)}{sample\ mass(g)} \tag{4.5}$$

Finally, combining Equations (4.2), (4.4) and (4.5), the EE efficiency of CMHEC is calculated as

$$\%EE = \frac{Total\ Analyte - \left[\left(10^{\frac{Log\left(\frac{Peak\ Area}{B}\right)}{A}}\right) * \frac{dilution(mL)}{mass(g)}\right]}{Total\ Analyte} * 100 \tag{4.6}$$

4.2.2 Total Nitrogen Analysis

For the cement slurries studied in this investigation, PEI acts as a secondary fluid loss additive and also significantly contributes to viscosity of the mixture. Therefore, it was necessary to develop a method to assay the entrapped PEI. Although the HPLC system previously discussed would have been an ideal candidate to simultaneously measure CMHEC and PEI, peak interference compounded by low response factors made quantitation of PEI unfeasible. Instead, a dual total organic carbon/total nitrogen (TOC/TN) instrument was used (Shimadzu TOC-L Analyzer, Shimadzu Corporation, Kyoto, Japan). See figure 4.6. In the PEC systems studied here, only PEI contains atoms of nitrogen, which makes the TN portion of the instrument useful for determining the EE.

Figure 4.6 Shimadzu TOC/TN analyzer

The analysis of TN is based on the theory of catalytic decomposition of nitrogenous compounds to NO (nitric oxide) through thermal oxidative pyrolysis. Practically all nitrogen found in an aliquot of sample is decomposed to NO as it passes through the furnace and catalyst bed. A carrier gas transports the unstable NO to a gas analyzer where it reacts quickly with ozone to form NO_2 (nitrogen dioxide). This reaction produces light in a process known as chemiluminescence. The produced photons stimulate a photodiode creating a voltage that can be read by the computer. Because the size of this voltage spike is proportional to the concentration of nitrogen in the sample, the final PEI concentration can be determined by comparing to a known standard (Shimadzu TOC-L analyzer manual, July 2013; Avramidis et al., 2015).

Since this method does not discriminate against the form of nitrogen, as long as it can be thermally decomposed under these conditions, the total amount of PEI in the

sample can often be measured without any additional sample preparation. Free PEI can be determined by centrifuging the mixture to remove the nanoparticles prior to analysis on the analyzer. Finally, the EE of PEI is calculated from Equation (4.2), similar to that of CMHEC.

4.2.3 Dynamic Light Scattering

The Brookhaven NanoBrook Omni DLS (Dynamic Light Scattering) instrument, shown in Figure 4.7, was used to determine the particle size and zeta potential of the PEC nanoparticles (Brookhaven Instruments Corporation, Holtsville, NY).

Figure 4.7 NanoBrook Omni DLS particle sizer and zeta potential analyzer

The DLS follows principles similar to the ELS detector previously discussed. For size determination, a beam of monochromatic light, such as from a laser, is impinged upon a dilute solution containing nanoparticles. The particles cause the light to scatter in all directions according to Raleigh or Mie scattering theory. A detector is set up at a specific angle, typically 90° relative to the incident beam, to capture this scattered light.

As the particles move freely in solution, according to Brownian motion, the light reaching the detector will fluctuate in intensity at a given frequency relative to the particle's radius (Sartor, 2003). A schematic of this is shown in Figure 4.8.

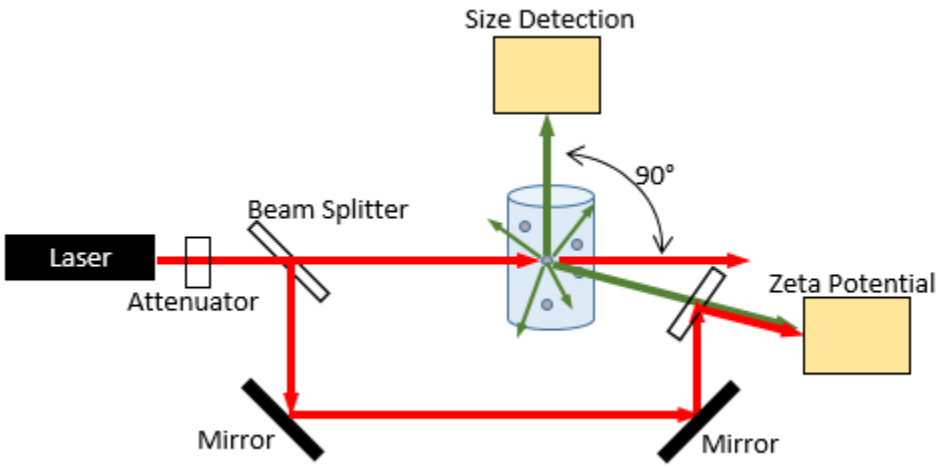


Figure 4.8 Schematic of DLS optics

Zeta potential is a characteristic describing the surface charge on a particle and helps describe the particle's colloidal stability in solution. Particles with larger absolute zeta potentials will tend to have higher electrostatic repulsion and will produces more stable suspensions. Alternatively, particles with low absolute zeta potentials will tend to agglomerate and settle. Typically, a suspension is considered stable when the absolute value of the zeta potential is greater than approximately 20-25mV.

To measure the zeta potential, an electric field is applied to the sample causing the particles to move with a given velocity relative to its surface charge. Again, a beam of light is scattered off of the particles and is detected by a photomultiplier. In this case, the light waves experience a phase shift with respect to a standard source as it bounces

off the particles moving in solution. By observing the intensity of light, the phase shift can be established followed by the velocity of the particle. Finally, based on the particle's velocity in a known electric field, the zeta potential can be calculated (Miller et al., 1991). This is also shown in Figure 4.8.

The provided PEC solutions are prepared for measurement by first subjecting them to an ultrasonic bath for several seconds to break up any particles that may have agglomerated. Next, the samples must be diluted to a sufficient degree to ensure the right number of scattered photons reach the detector. Too few particles means insufficient light, and therefore data, for an accurate measurement. Too many particles may result in either saturation of the detector or they may interfere with the transmission of light through the medium, such as occurs in optically turbid solutions. The number of photons reaching the detector is tallied and recorded in kilocounts per second (kcps). The instrument will automatically attenuate the laser intensity to obtain a count rate within a predetermined range. Even at 100% laser transmission, if the count rate is below 50-100kcps, the sample is too dilute for an accurate measurements. For the PEC systems studied here, an ideal concentration is often obtained by diluting 4 drops of sample in enough deionized water to fill the cuvette to approximately ¾ full.

Since the equations governing the calculation of particle size and zeta potential are strongly dependent upon temperature, it is important to allow the samples to equilibrate before measurement. For most determinations, the temperature is set to 25°C. The computer software perform all necessary correlations and calculations and outputs the information for particle size, count rate, and zeta potential.

4.3 Cement Slurry Characterization

4.3.1 Slurry Preparation and Conditioning

Prior to any test being performed, the cement slurry must be prepared and conditioned following the standards outlined in API RP 10B-2 for Class H cement. According to regulations, 860g of cement is to be mixed with 327g of water (38%) (API Spec 10A, 2010). The mix water and any liquid additives are first placed in the blender. The dry cement components and additives are then added uniformly to the fluid within 15 seconds maximum while the blender rotates at 4,000 rpm. After all components have been added, the mixture is then ramped up to 12,000 rpm and left to mix for 35 seconds. The high speed blender used for this study is shown in Figure 4.9 (Model 20 constant speed blender, provided by OFI Testing Equipment Inc., Houston, TX)

Figure 4.9 OFITE high speed blender

After mixing, the slurry is then quickly loaded into a consistometer cell that is outfitted with a paddle and lid, see Figure 4.10.

A  B 

Figure 4.10 (A) Chandler consistometer (B) conditioning cell with paddle and lid.

The cell is then placed into the water bath of the consistometer, which has previously been heated to the desired testing temperature, and the instrument is turned on (consistometer provided by Chandler Engineering, Houston, TX). The cement slurry is left to condition for 30 minutes at 150 rpm. After conditioning, the prepared slurry is ready for testing. Note, the instrument used here is an atmospheric-type consistometer so the temperature must be maintained below 88°C to prevent the contents of the solution from boiling off (See API RP 10B-2).

4.3.2 Static Fluid Loss

The aim of the fluid loss test, as the name implies, is to provide a procedure that measures the slurry's ability to control fluid loss under controlled conditions. The test is executed based on API RP 10B-2 using a high temperature, high pressure (HTHP) filter press, shown in Figure 4.11A (OFI Testing Equipment, Houston, Texas). In this procedure, the pre-conditioned cement mixture is loaded into the HTHP cell (see Figure 4.11B) that has previously been equilibrated to the desired temperature.

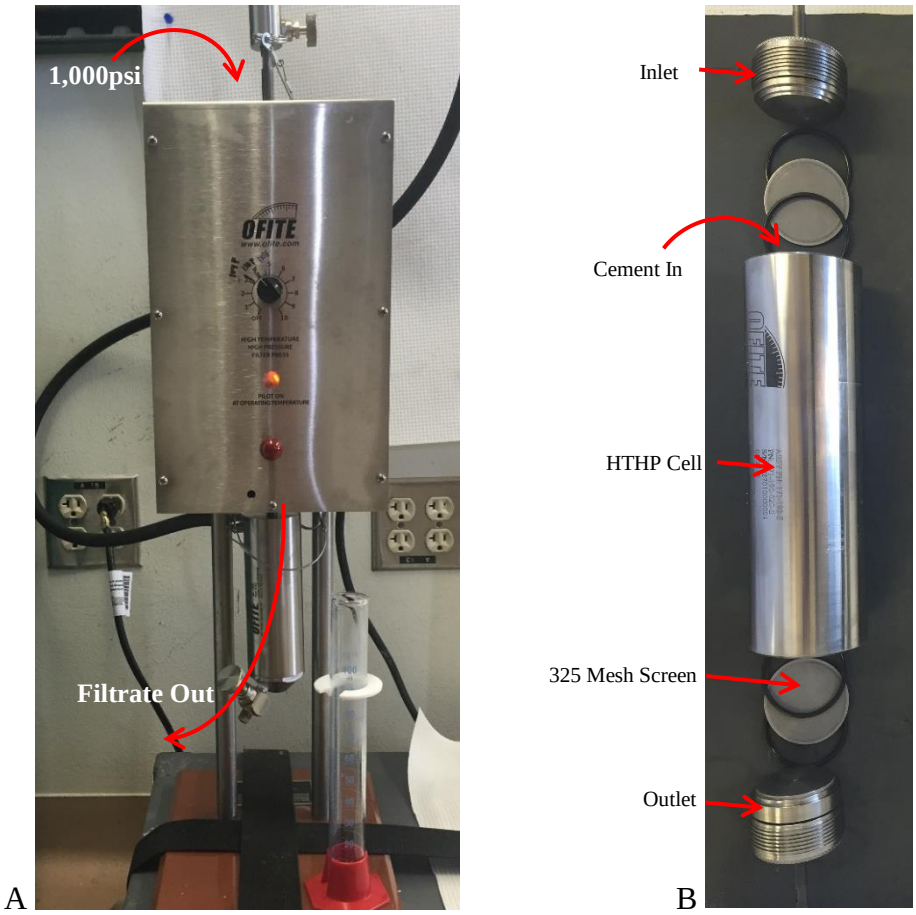


Figure 4.11 (A) OFITE filter press, (B) HTHP cell components

Inside the cell, the cement sits on top of a size 325 mesh (45μm opening) metal screen that is intended to simulate the pores of the rock formation encountered underground. A pressure of 1,000psi is applied to the inlet of the cell using $N_{2\,(g)}$. This forces the cement against the screen while the outlet is left at atmospheric conditions to create a pressure differential of 1,000psi. The test begins as soon as the pressure is applied. The filtrate is then collected and measured at intervals of 0.5, 1, 5, 10, 15, 20 and 30 minutes. The final API reported volume is determined by doubling the total volume collected in the 30 minute time period (API RP 10B-2). If at any time during the procedure nitrogen is observed to channel through the system causing a "blow through," the test is stopped. The total volume of filtrate collected at that time is then used in Equation (4.7) to obtain the reported calculated API fluid loss.

$$Calculated\ API\ Fluid\ Loss\ (mL/30min) = 2V_t\sqrt{\frac{30}{t}} \tag{4.7}$$

Here, 'V_t' is the volume of filtrate collected at the time of blow through in mL and 't' is the elapsed time in minutes (API RP 10B-2).

Under the previously stated conditions, the test can be performed at temperatures between room temperature and 88°C. If the desired testing temperature is above 88°C, a backpressure needs to be applied at the outlet according to Table 4.4 to prevent the water from vaporizing in the cell (OFITE HTHP Filter Press with Threaded Cells User Manual, December 2015). Simultaneously, the inlet pressure must be increased to maintain the 1,000psi differential between the outlet and inlet.

Test Temperature		Vapor Pressure		Minimum Back Pressure	
°F	°C	PSI	kPa	PSI	kPa
212	100	14.7	101	100	690
250	121	30	207	100	690
300	149	67	462	100	690
350	177	135	932	160	1,104
400	204	247	1,704	275	1,898

Table 4.4 Recommended minimum back pressure for various temperatures (OFITE HTHP Filter Press with Threaded Cells User Manual, December 2015)

After the fluid loss test is performed, the cell is disassembled, taking care to preserve the filter cake that has formed on the lower screen. The thickness and physical properties of the filter cake are recorded and may be used for comparative purposes. (See Figure 4.12)

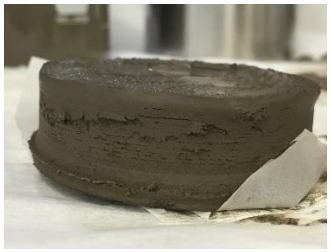
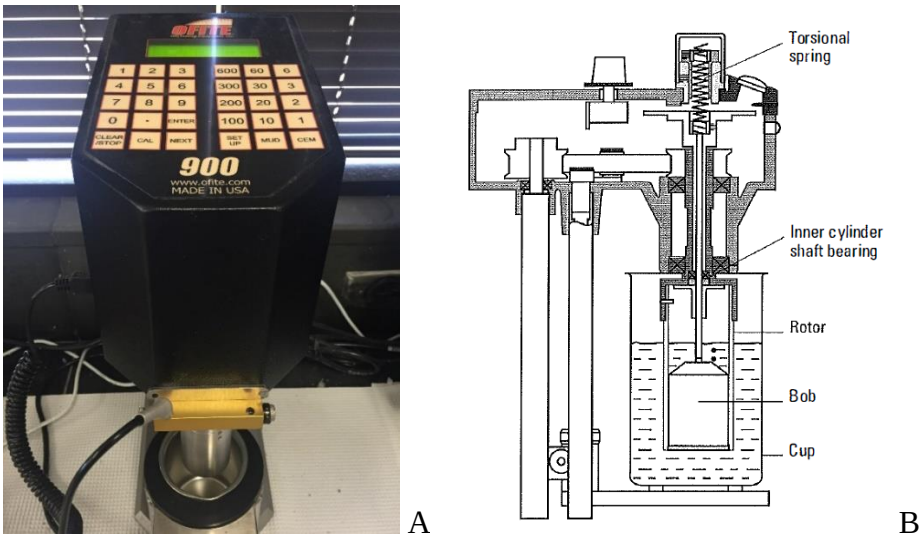


Figure 4.12 Filter cake extracted from cement screen after fluid loss test

4.3.3 Rheology

The OFITE model 900 rotational viscometer (OFI Testing Equipment, Houston, TX) was used for measuring all rheological properties of the cement slurries in this investigation (See Figure 4.13 A). The procedure follows API guidelines RP 10B-2 using a "bob and sleeve" setup. A schematic of the viscometer is given in Figure 4.13 B.



A B

Figure 4.13 (A) OFITE viscometer and (B) schematic (API RP 10B-2)

Measurements are performed at increasing shear rates of 3, 6, 30, 60, 100, 200 and 300 rpm and a second time from the top down to provide two data points for each step. Using the Bingham Plastic fluid model, the plastic viscosity (PV) and yield point (YP) are determined. The Bingham Plastic model assumes a linear relationship between sheer rate and shear stress with an offset corresponding to the YP. According to this model, the following equation can be produced to relate the measured sheer stress to the plastic viscosity.

$$\tau = YP + (PV * \gamma) \tag{4.8}$$

Where 'τ' is the sheer stress in Pa, YP is in Pa, PV is in cP, and 'γ' is the sheer rate in sec^{-1} (API RP 10B-2). These values are used quantitatively to compare the viscosities and yield stresses of the various samples.

Immediately following the viscosity measurements, gel-strength tests are performed; first with a 10 second static period followed directly by a 10 minute static

period. Although this gel-strength test is useful for comparisons, it is not meant to be used in place of the API's recommended static-gel-strength (SGS) procedure. Because a SGS instrument is not available, the gel strengths measured using this viscometer must suffice for understanding the gel strength development.

4.3.4 Free Fluid

The free fluid test was also performed following API RP 10B-2. This procedure provides a means of measuring the stability of a cement slurry with regard to settling and sedimentation. The procedure is performed by pouring a previously prepared and conditioned slurry into a graduated cylinder meeting the required dimensions set by the API. The slurry fill length to inside cylinder diameter ratio must be between 6:1 and 8:1 with a slurry volume between 100 and 250mL (API RP 10B-2). The container is then sealed to prevent evaporation and is left at the desired temperature for 2 hours in a vibration free environment. An example of the prepared sample is given in Figure 4.14.


A


B

Figure 4.14 Free fluid test. A – Graduated cylinder with slurry. B – Free fluid that has developed on top of the slurry after 2 hr. incubation.

After the 2 hour sitting time, the free fluid that has developed on top of the slurry is measured and recorded as a percentage of the original slurry volume using Equation (4.9).

$$\varphi = \frac{V_f}{V_s} * 100 \tag{4.9}$$

Here 'φ' is the volume fraction of free fluid as a percentage, 'V_f' is the volume of free fluid collected in mL, and 'V_s' is the initial volume of the slurry in mL.

The API has stipulated that a slurry's free fluid must be less than 5.9% to be suitable (API Spec 10A, 2010). Some consider this value to be too high, arguing that the development of much more than a trace amount of free water is unacceptable, especially for deviated or horizontal wells (Salehi et al., 2009; Devereux, 1998). For the present study, a result of 0.5% was taken to be the maximum allowable value for a slurry to be considered stable, as recommended by Devereux (Devereux, S., 1998).

4.3.5 Density

Density is an important characteristic of a cement slurry because it is the parameter that determines the amount of hydrostatic head the cement column can exert (See Equation (1.1)). Unlike the other procedures mentioned above, there is no unique result range or specification sought for this test. For real life, practical applications, density must be adjusted to match the appropriate downhole conditions with the use of additives such as bentonite, hematite and barite (Mitchell et al., 2011). Here, the test is performed for the purpose of due diligence and to ensure there are no significant fluctuations resulting from the combinations of additives used. The procedure is performed following API specifications (API RP 10B-2) using the OFITE pressurized fluid density balance shown in Figure 4.15 (OFI Testing Equipment, Houston, TX).

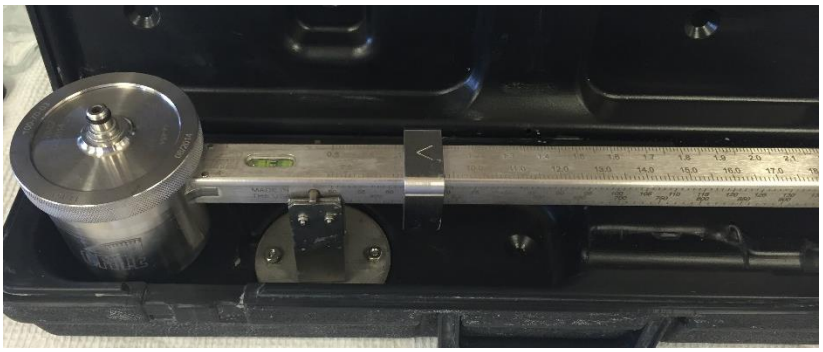


Figure 4.15 OFITE pressurized fluid density balance

First, the cup is filled nearly to the top with slurry and the cap is screwed down tightly. Any remaining empty space in the cup is then filled with slurry using the check valve on top. A piston is used to inject fluid through the valve and pressurize the cup. The valve will close when sufficient pressure is applied. A pressurized balance is

preferred as it minimizes errors relating to small amounts of entrained air by compressing the air bubbles until their size is negligible. Once filled, the balance assembly is placed in the knife edge and the sliding weight is adjusted to find the balancing point. The edge of the adjustable weight indicates the density value that is scribed on the pre-calibrated ruler.

4.3.6 Thickening Time

As with all other slurry testing procedures, the thickening time test follows API standards. This test uses the consistometer and container previously mentioned for conditioning the slurry. Instead of removing the slurry from the instrument after 30 minutes, however, the slurry is left mixing to observe how long it remains fluid and flowable. A potentiometer built into the lid of the mixing cell continuously measures the thickness of the mixture in Bearden units of consistency, B_c. For perspective, many regard cement slurries as unpumpable at approximately 30-40 B_c (Van Kleef et al., 1993; Purvis et al., 1993). A picture of the potentiometer is given in Figure 4.16. Note, the markings on this consistometer must be multiplied by 10 to convert to B_c units.

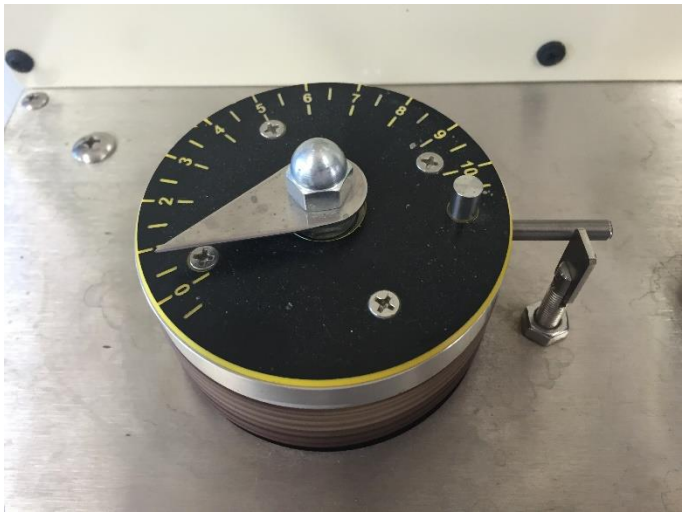


Figure 4.16 Potentiometer

Specifications for thickening time under HTHP schedules are given by the API (API Specification 10A, 2010). Under these conditions, the thickening time is defined as the time taken to reach 100 B_c. No such specification is given, however, for the atmospheric-pressure type consistometer used in this study. For the purpose of this investigation, the data is merely used for comparative purposes. Therefore, the test was allowed to proceed only for approximately 5 hours, with data collected intermittently, so a useful thickening profile could be obtained. This provided enough information to make useful comparisons between slurry compositions. Note, standard H class cement was used as a baseline for the study.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Entrapment Efficiency of CMHEC by HPLC

This section describes the results of the EE of CMHEC using HPLC under the conditions stated above in Table 4.2. Figure 5.1 gives an example of a calibration curve that was created using CMHC standards of 25, 50, 100, 150, 200, and 250ppm. Using a power law curve, a correlation coefficient of 0.9999 was obtained, demonstrating an excellent fit with the data. The fitting parameters for 'A' and 'B' were 1.70098 and 0.29027 respectively giving a calibration curve of $y = 0.29027x^{1.70098}$. The remaining calibration data is given in Table 5.1.

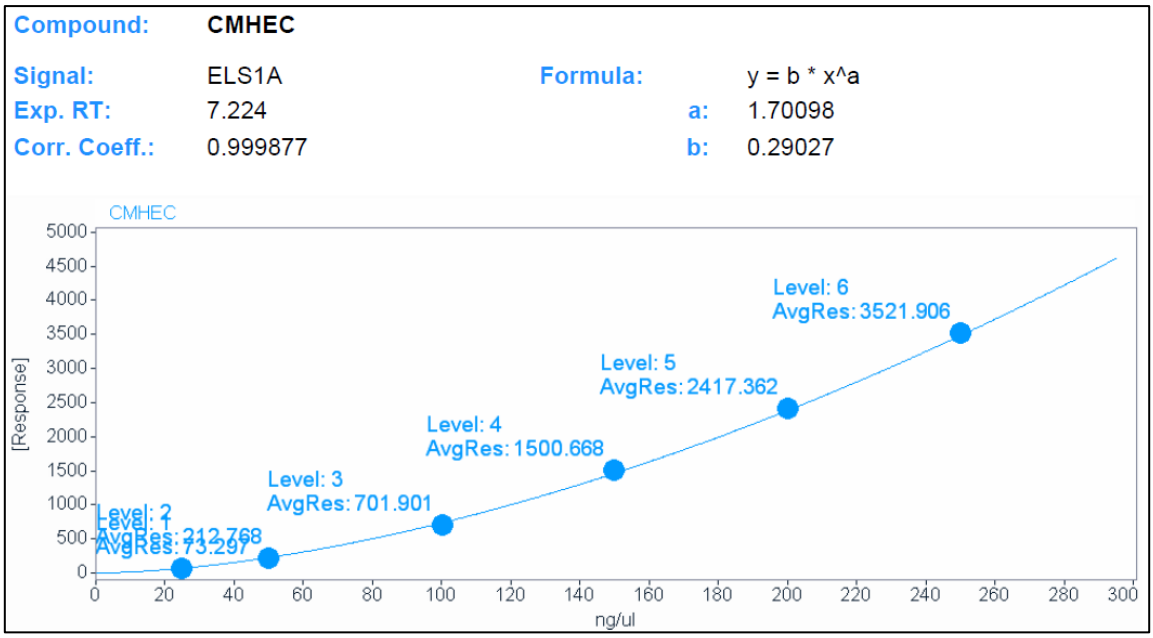


Figure 5.1 Example CMHEC calibration curve

Sample	Prepared [CMHEC] (ppm)	Retention Time (min)	Peak Area (Counts)	Tailing Factor	Equation & Fitting Parameters
25ppm STD	25.01	7.24	73.30	1.4	
50ppm STD	50.20	7.22	212.77	1.3	y = B*x^A
100ppm STD	100.25	7.24	701.90	1.2	A = 1.70098
150ppm STD	149.98	7.24	1500.67	1.2	B = 0.29027
200ppm STD	200.02	7.25	2417.36	1.2	
250ppm STD	249.90	7.25	3521.91	1.2	

Table 5.1 HPLC calibration data

To ensure selectivity of the system for CMHEC, control samples of PEI (300ppm) and PAA (100ppm) were injected on the column along with a standard of CMHEC (100ppm). Figure 5.2 shows an overlay of these three chromatograms.

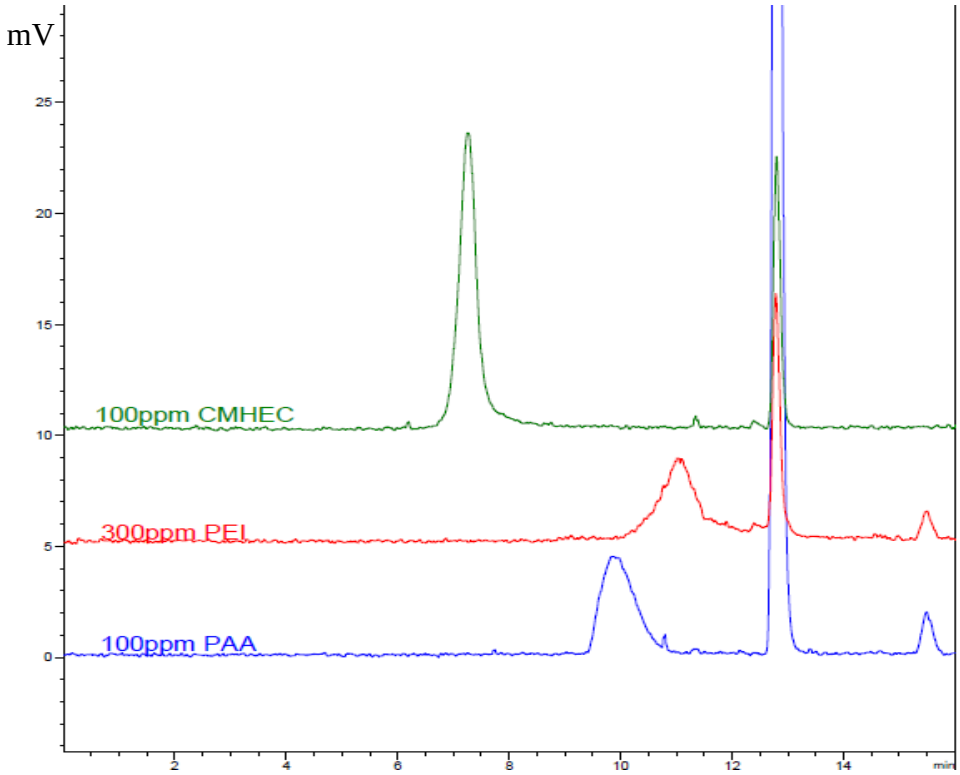


Figure 5.2 Chromatogram overlay of CMHEC, PEI and PAA peaks

From this figure it can be easily seen that there is an ideal amount of separation between the most prominent peak of CMHEC, eluting at approximately 7.25 minutes, and peaks of any other analyte. Interestingly, the retention time of PEI is longer than that of CMHEC. This is contrary to the logic of SEC in which larger molecules are expected to elute first. One possible explanation is that, under the alkaline conditions of the buffer, PEI is non-ionic. Without the electrostatic repulsion between its branches, the molecule may therefore exist in a folded or packed conformation. This action reduces its hydrodynamic radius causing it to flow more slowly through the column. Alternatively, CMHEC exists as a highly anionic molecule at high pH. In combination with the molecule's linear rigidity, it is theorized that the negatively charged functional groups repel one another causing the molecule to be fully extended. This increases the molecule's hydrodynamic radius and causes it to elute more rapidly. Another possibility is that the PEI has some affinity to the column more than that of CMHEC causing it to be retained longer. Regardless of the mechanism, the chromatographic overlay gives confidence in the ability to quantitate CMHEC without fear of interference from PEI or PAA.

A sample chromatogram of the PEC solution is shown in Figure 5.3.

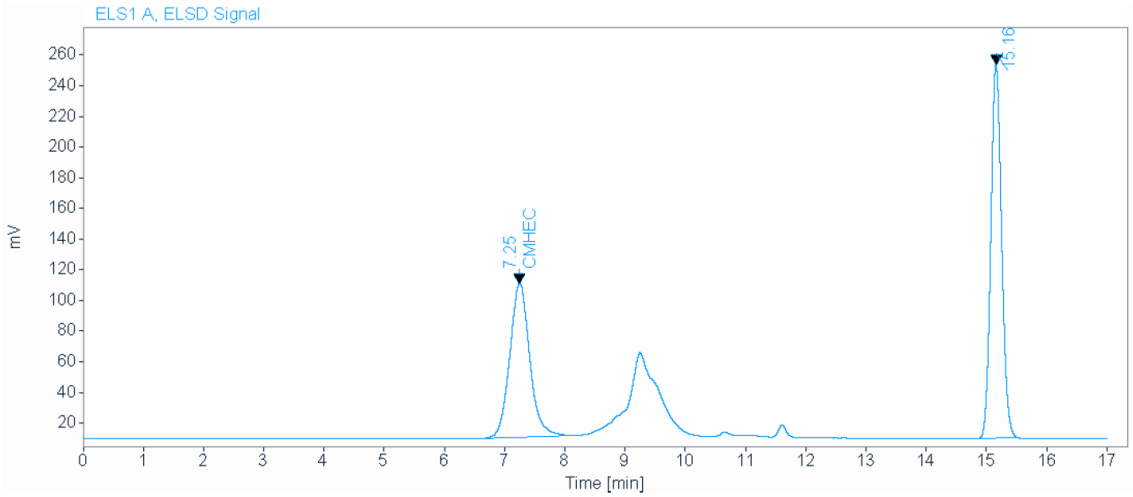


Figure 5.3 Sample PEC chromatogram

The average calculated EE of this sample was -8.5 ± 1.0%, indicating that more CMHEC was recovered than was in the original sample. This is obviously not theoretically possible. Upon further scrutiny, it was discovered that the centrifugation step produced a large, dense pellet that covered approximately 15% tube's volume (assuming ~0.3mL of pellet in a 2.0mL total volume microcentrifuge tube). See Figure 5.4 for a photograph of the observation. The pellet may be difficult to see in the picture but its bounds are indicated with red markings.

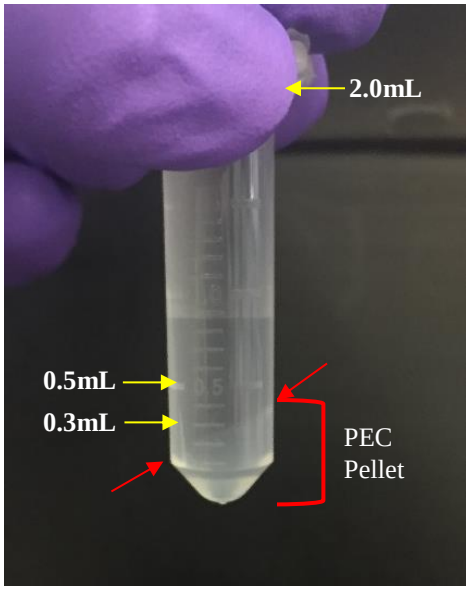


Figure 5.4 Centrifuged PEC sample with pellet

Assuming the pellet contains concentrated nanoparticles, and little if any free CMHEC, this means that the remaining sample is approximately 15% more concentrated. If this is assumption is accurate, re-working the calculations gives a reasonable calculated value of 7.8% for the EE of CMHEC. To verify this hypothesis, a sample was prepared and tested in the same fashion as before but omitting the centrifugation step. This ensured that the entire sample was homogenous. The resulting chromatogram is shown in Figure 5.5.

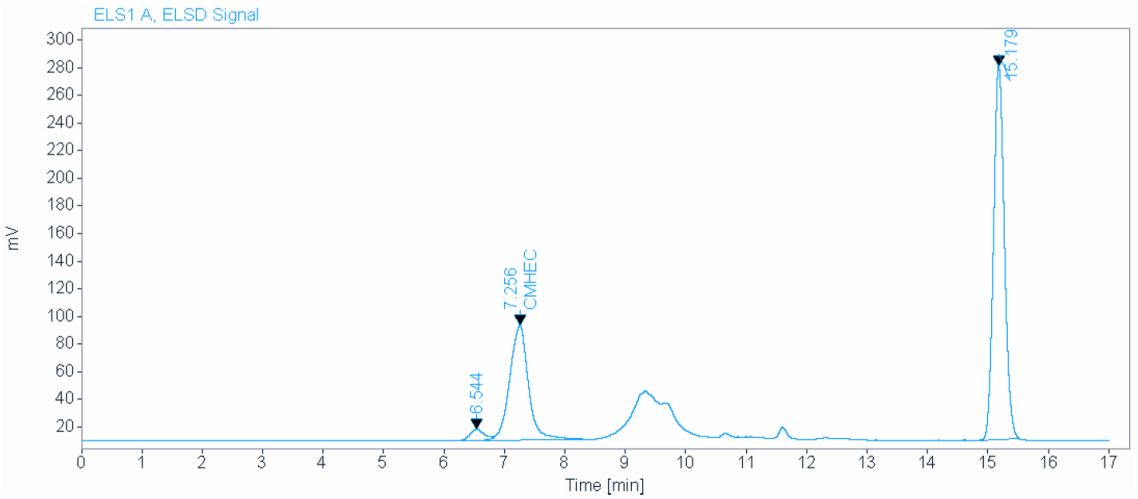


Figure 5.5 Example PEC chromatogram with no centrifugation

Notice that by not removing the nanoparticles through centrifugation, the sample chromatogram contains an additional peak that elutes just before the CMHEC peak with slight overlapping. This small peak corresponds to PECs that are larger than CMHEC molecules but smaller than the 0.45µm filter used to filter the sample. Therefore, they are pushed through the column more rapidly than CMHEC. Although the tail of the PEC peak overlaps slightly with that of the CMHEC, there is enough resolution that accurate calculations can be made. The resulting EE of this sample was 7.4%, consistent with the original sample after correcting for the concentrating effect.

To further substantiate this result, a fresh PEC solution was prepared and tested, again without centrifugation. This PEC preparation is referred to as "Solution #2." The average EE of this new sample was 10.8 ± 0.1%. This is again reasonably consistent with prior results and adds validity to the method. The increase from 7.4% to 10.8% EE can be explained simply by the age of the sample. PEC Solution #1 had been prepared several weeks prior to injection while Solution #2 was prepared the day before it was

tested. Experience has shown that these nanoparticles will begin to dissociate over time, leading to the lower EE of Solution #1. Because of this, the average result from Solution #2 will be taken as the actual EE of this PEC. All relevant sample data is summarized in Table 5.2.

Sample	Sample Mass (g)	Inj. #	Retention Time (min)	Peak Area (Counts)	Tailing Factor	%EE	**Average**
PEC Soln. #1	2.011	1	7.26	2378.98	1.15	-9.34	**-8.5**
		2	7.25	2315.78	1.11	-7.62	
15% Correction						7.8	**7.8**
*PEC Soln. #1 (No Centrifuge)	2.005	1	7.26	1783.16	1.05	7.43	**7.4**
**PEC Soln. #2 (No Centrifuge)	2.119	1	7.23	1834.51	1.31	10.87	**10.8**
		2	7.24	1838.46	1.26	10.76	

*Note: Only one injection of this sample was performed
**Note: Sample tested on different day. Curve: $y = 0.21292x^{1.76096}$, Correlation Coefficient: 0.9997

Table 5.2 HPLC sample test data.

Although 11% EE for CMHEC seems rather low, it does appear to be consistent with current understanding and observations. During sample preparation, cationic PEI and anionic PAA solutions are mixed first followed shortly by the anionic CMHEC polymer solution. Because PEC formation occurs rapidly, owing to the electrostatic interactions, it is very reasonable to assume that most of the active sites on PEI are consumed immediately upon addition of PAA. With very little positive charge left on the molecule, there is not much availability for CMHEC to react once it is added to the mixture. The cellulose molecules that do react are then expected to bind more loosely on the outside of the PEC core formed first between PEI and PAA (See Figure 5.6).

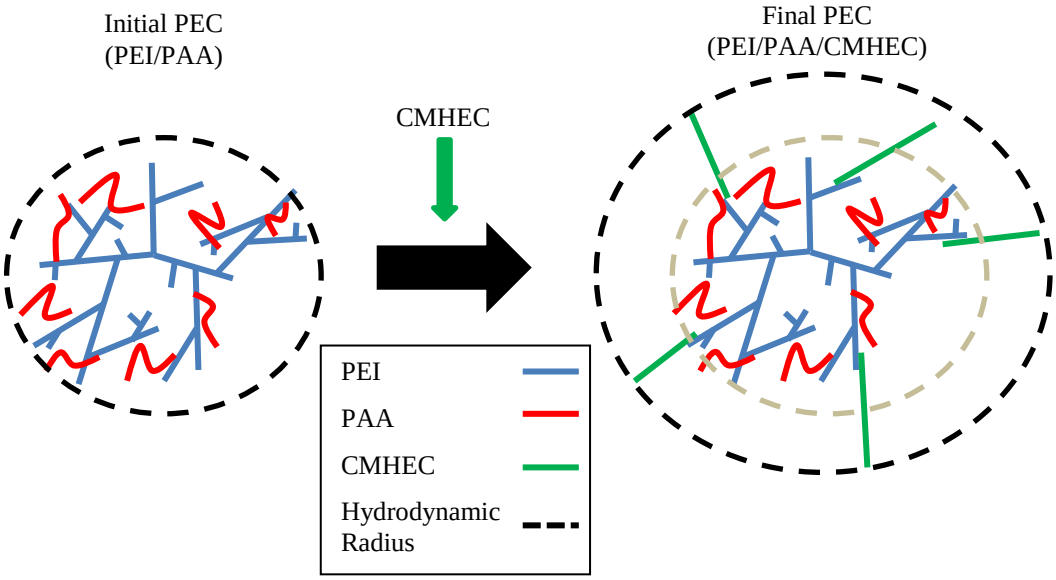


Figure 5.6 Mechanism of PEC formation

This logical assumption is also supported visually. During the initial PEC preparation step, with just the addition of PEI and PAA, the solution immediately becomes somewhat translucent or slightly cloudy. This visual cue is indicative of PEC formation. Upon addition of CMHEC, however, very little change is observed. This is in contrast to solutions formed between PEI and CMHEC alone where a noted change occurs immediately through the formation of a thick, heavy, aggregate. This further suggests that little CMHEC is being entrapped in the nanoparticle complex. Despite the low EE, however, it is shown below that this small amount of entrapped CMHEC results in a significant increase in fluid loss control.

5.2 Entrapment Efficiency of PEI by TN Analysis

The EE measurement of PEI was performed by Dr. Y.Y. Lin with a resulting value of 27.3%. In conjunction with the CMHEC data previously given, this outcome

further establishes that nanoparticles can indeed be formed using these common oilfield polymers. This finding is essential as it satisfies one of the primary objectives of the thesis; to form a PEC from CMHEC, PEI, and PAA.

With approximately one fourth of the PEI entrapped, it is expected that the viscosity of the system would decrease while still providing a sufficient amount of free PEI to aid in fluid loss control and slurry stability. A comprehensive discussion on the rheology and stability of the PEC system is provide in their respective sections below.

5.3 Particle Size and Zeta Potential

The nanoparticle system used in these experiments was tested for particle size and zeta potential by Dr. Y.Y. Lin with the following values: particle size = 144 ± 0.8nm, count rate = 463 ± 34kcps, zeta potential = -23 ± 1.0mV. Although the particle size is slightly above what may traditionally be considered the limit for the nano-scale (<100nm) the size is still small enough to reasonably be considered a nanoparticle. In addition, with a count rate well above 400 kcps, it can be concluded that there was sufficient data collected to achieve an accurate measurement of the particle size.

As for the zeta potential, the result indicates that the solution contains a reasonable degree of stability. A stable slurry is considered to have an absolute value of greater than 20-25 mV. This is confirmed visually by observing that a translucent, slightly colored mixture is obtained. When allowed to sit overnight, however, the particles settle to the bottom suggesting that this is not a completely stable colloidal

suspension. Regardless, colloidal stability is not a major concern as long as the nanoparticles perform their intended functions once added to the cement slurry.

To confirm the mechanism of PEC formation described in Figure 5.6, a new nanoparticle suspension was prepared consisting of only PEI and PAA. The resulting solution appeared visually similar to that of the original PEC. This indicates that nanoparticles are indeed formed between these two components alone and confirms the first part of the proposed method. This mixture was then tested for particle size and zeta potential with results of 117 ± 1.0nm and -17 ± 1.2mV, respectively, at a count rate of 493 ± 15kcps. The fact that this two component system produced smaller particles than the normal PEC (144 nm) further supports the second part of the theorized mechanism. In other words, when CMHEC is entrapped, the hydrodynamic radius of the particle is expected to be larger. Finally, the difference in zeta potential between the two mixtures further validates the theory. A PEC that contains negatively charged CMHEC molecules is expected to have a larger negative zeta potential than the same PEC without them.

5.4 Static Fluid Loss

Varying concentrations of CMHEC as PEC nanoparticles were used in cement slurries to test for their fluid loss capabilities. Table 5.3 summarizes the main results for tests performed at 40°C. Control samples were also tested using raw materials of CMHEC, PEI, and PAA for comparisons. An explanation of these results follows.

Test #	% CMHEC (bwoc)	% PEI (bwoc)	% PAA (bwoc)	CHMEC in PEC?	API Fluid Loss (mL/30min)
1	0	0.3	-	-	1320 ± 134
2	0	-	0.3	-	1850 ± 188
3	0	0.36	0.18	-	863 ± 109
4	0.1	0.18	0.09	X	478 ± 25
5	0.1	-	-	-	1673 ±143
6	0.15	0.27	0.135	X	91 ± 9
7	0.2	0.36	0.18	X	52 ± 8
8	0.2	0.36	0.18	-	161 ± 51
9	0.2	-	-	-	216 ± 11
10	0.25	-	-	-	169 ± 17
11	0.3	0.54	0.27	X	38 ± 11
12	0.3	-	-	-	92 ± 9
13	0.35	-	-	-	72 ± 7
14	0.4	-	-	-	53 ± 5
15	0.5	-	-	-	36 ± 4
16 (Halad-9)	-	-	-	-	26 ± 4

Table 5.3 Summary of API fluid loss data at 40°C

Not too surprisingly, in moderate concentrations (0.3%bwoc), both PEI and PAA individually showed no fluid loss control capabilities (Test #1 and Test #2 respectively). In fact, both tests experienced a blow through of nitrogen in less than 1 minute with calculated API fluid loss values much greater than 1,000 mL/30min. This is expected, as neither compound alone is known to be useful at controlling fluid loss at these concentrations. We can conclude that neither PEI nor PAA can provide fluid loss control under these conditions. For comparison, 0.3% CMHEC as a raw material produced a fluid loss of 92 ± 9mL/30minutes (Test #12). This was determined to be the lowest concentration required that could still comply with the API specification of ≤

100mL/30minutes. These test results will be used as a baseline for studying the PEC system.

In contrast to the three control samples mentioned above, when 0.3% CMHEC as a PEC was used in the cement slurry, the fluid loss was only 38 ± 11 mL/30minutes (Test #11). This means it is over twice as effective at controlling fluid loss as the raw material alone. In order for the raw material to achieve the same control, it would require approximately 0.5% (Test #15). Furthermore, only 0.15% of CMHEC as a PEC (Test #6) was required to achieve acceptable API fluid loss compared to the 0.3% required of the raw material (Tests #12). This is very significant as the PEC system demonstrates a 50% reduction in amount of CMHEC FLA required to meet the industry standard.

From this data we can conclude that a combination of PEI, PAA, and CMHEC can provide exceptional fluid loss control. However, the objective is to establish that the PEC nanoparticles can control the fluid loss and not just a random combination of these three individual components. To explain, it is reasonable to postulate that all polymers could be released from the PEC immediately upon being mixed in the highly basic and highly saline conditions of the slurry. Then, in some unexplained and inconsequential fashion, the free molecules contribute to the control observed. If this were the case, there would be no reason to form a PEC and the goal of the thesis would not be satisfied. This is especially relevant considering the low EE of the CMHEC FLA discussed previously. Therefore, further investigation was needed.

To verify that indeed the PEC entrapping CMHEC provides the control and not just a combination of these three components, another control test was devised. In this test (Test #8 in Table 5.3), the CMHEC was not included as a component of the PEC yet was still added to the slurry at 0.2% bwoc. The liquid portion of the slurry was comprised of the appropriate amounts of PEI and PAA in water (0.36% and 0.18% respectively), expectedly forming PEC nanoparticles during mixing. Instead of being trapped in a nanoparticle, however, the 0.2% CMHEC was dispersed in the dry cement mixture. This ensured that all polymers existed in the slurry in their appropriate ratios but reduced the probability of CMHEC being entrapped. The results from this test were then compared to 0.2% CMHEC as PEC and 0.2% CMHEC as raw material. The findings are summarized in Figure 5.7.

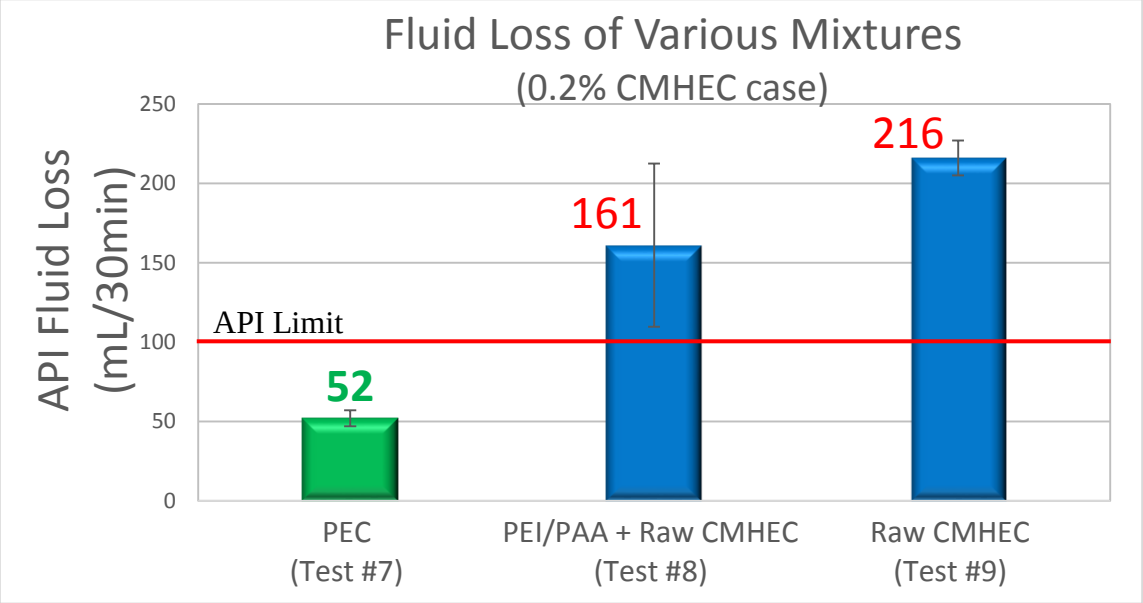


Figure 5.7 API fluid loss of three different mixtures containing 0.2% CMHEC. 1) Mixture containing the developed PEC system; 2) Mixture containing all components but not in a normal PEC; 3) Mixture containing only CMHEC as raw material

Three determinations of this control sample were performed with resulting API fluid loss values of 208, 168, and 106 mL/30min (Note: the average value of 161 mL/30min is recorded as the result for Test #8 in Table 5.3). The variability in the data is likely due to the complexities of the slurry preparation. As previously discussed, PEC formation depends heavily on numerous factors that, under isolated conditions, are easy to control. However, when adding the CHMEC interlaced cement, it is nearly impossible to control all of the variables that might affect the polymers' interactions. For example, if CMHEC molecules are mixed near the top of the dry cement, they will be among the first particles to mix with the liquid. This could result in some CMHEC being entrapped in the PEC and may explain minor improvements in fluid loss control. It must be noted that these fluctuations do not appear affect the reliability of the other data points collected in this study. All other values reported either fit expected trends or have been shown to be reproducible.

Regardless, the variations of this control sample are not a significant concern. The important fact is that, on average, the normal PEC system performed over three times better than the control test. This provides strong evidence that the developed PEC system, with entrapped CMHEC, is indeed responsible for providing the excellent fluid loss capabilities observed. This conclusion is further supported by the results of Test #3 in Table 5.3, in which a PEC was made from just PEI and PAA alone. The polymer ratios in this test were chosen to be comparable to the 0.2% CMHEC as PEC case (Test #7). Again, in the absence of entrapped CMHEC, no acceptable fluid loss control is achieved.

The question still looming is, how can the entrapped CMHEC provide such superior control compared to the non-entrapped system when the EE is only 11%? The proposed answer is thought to lie in the structural characteristics of cellulose. Cellulose is made up of repeating glucose units attached through β(1,4)-linkages. This bond prevents the units from rotating causing cellulose polymers to be linear and non-branching. As discussed before, during preparation, CMHEC is expected to attach to the few remaining active sites on the outside of a PEC core formed by PEI and PAA. Therefore, it is proposed that when CMHEC is added to the mixture, the small PEI/PAA complex is expected to develop large needle-like appendages of cellulose that protrude outward from the particle (See Figure 5.6 above). Finally, since CMHEC is known to bind to the pores in the filter cake (Bülichen et al., 2012), the protruding ends would help the complex embed in the openings causing a plug to form, as shown in Figure 5.8 below.

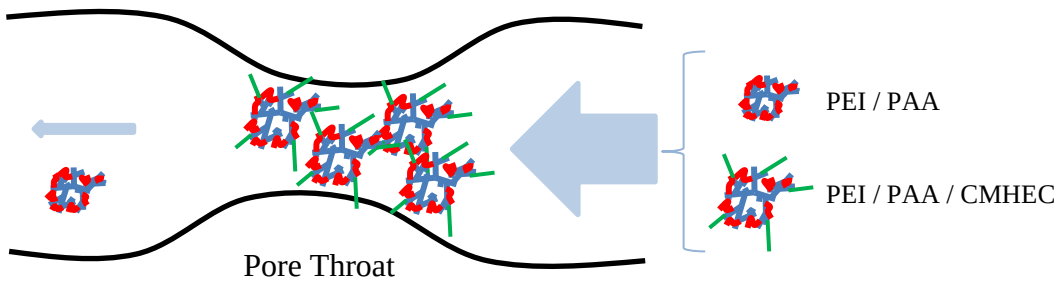


Figure 5.8 PEC pore blocking diagram

The free ends of the cellulose molecules may even bind to other nanoparticles creating a network of connecting PECs. This would greatly enhance its ability to plug the pores of the filter cake or even bridge multiple pores to achieve the fluid loss control observed.

The same PEC system was then tested at 65°C to observe how it would perform at higher temperatures. The data is found in Table 5.4.

Test #	% CMHEC (bwoc)	% PEI (bwoc)	% PAA (bwoc)	CHMEC in PEC?	Fluid Loss (mL/30min)
16	0.3	0.54	0.27	X	165 ± 17
17	0.3	-	-	-	148 ± 15
18	0.3	0.36	0.18	X	162 ±16
19	0.4	0.54	0.27	X	92 ± 9
20	0.4	-	-	-	88 ± 9

Table 5.4 Summary of API fluid loss data at 65°C

At elevated temperatures, the PEC did not perform as well as the control sample. At a concentration of 0.3% CMHEC, the fluid loss was out of specification with API requirements (Test #16). The slurry appeared visually more viscous and it gelled much more rapidly suggesting that the cement was curing too quickly. Since CMHEC is a known retarder and FLA, it was decided that additional free CMHEC could be included in the system to delay hydration and improve control. This was attempted at two different concentrations, recorded as tests #18 and #19 respectively. In test #18, the slurry was formed with only 0.2% CMHEC as a PEC and an additional 0.1% as raw material to hopefully improve the fluid properties of the slurry (Test #18). While the slurry rheology appeared to improve (whether because of more CMHEC or because of less PEC is not certain), no significant enhancement of the fluid loss control was seen. In Test #19, 0.3% CMHEC as PEC and 0.1% as raw material, for a total of 0.4% CMHEC, were added to the slurry. This resulted in an acceptable fluid loss of 92 ± 9

mL/30minutes. Although an improvement, this is still below the capabilities of the raw material alone at 0.4% (88 ± 9mL/30min, Test #20)

A reasonable explanation for the observed results is that, at elevated temperatures, the PEC dissociates into its individual components. With extra free PEI in the system, the slurry would definitely increase in viscosity. Although the free PAA is expected to act as a moderate friction reducer to prevent gel strength development, it exists in such a low concentration in the slurry that its effects are not seen. As a result of the high viscosity, the slurry becomes too rigid and is prone to bridging and gas channeling leading to low fluid loss control. Additional discussion on slurry viscosity at this temperature is given in section 5.5 below.

Unfortunately, concentrations of 0.4% CMHEC as PEC and higher are not possible with this system due to limitations on slurry water content. This shows one of the weaknesses of this system. However, these PEC nanoparticles still show promise for cementing shallow casing strings where the temperature is around 100°F or below.

5.5 Rheology

Cement rheology was also studied alongside the fluid loss tests at both 40°C and 65°C. First, data at 40°C will be considered. Table 5.5 summarizes the important data relating to PV, YP, 10 second gel strength, and 10 minute gel strength tests at this temperature.

Test #	% CMHEC	% PEI	% PAA	CHMEC in PEC?	PV* (cP)	YP (dyne/cm^2)	10s Gel (dyne/cm^2)	10m Gel (dyne/cm^2)
1	0	0.3	-	-	123.8	184.7	104	116
2	0	-	0.3	-	27.2	14.3	17	24
3	0	0.36	0.18	-	83.1	137.0	93	211
4	0.1	0.18	0.09	X	68.1	59.0	47	102
5	0.1	-	-	-	58.4	98.9	63	88
6	0.15	0.27	0.135	X	101.8	43.3	31	130
7	0.2	0.36	0.18	X	118.0	1.8	4	25
8	0.2	0.36	0.18	-	149.2	22.9	21	48
9	0.2	-	-	-	69.1	0.0	0	15
10	0.25	-	-	-	83.7	25.7	23	105
11	0.3	0.54	0.27	X	241.9	46.4	28	88
12	0.3	-	-	-	115.3	4.1	8	34.5
13	0.35	-	-	-	145.5	2.1	11	61
14	0.4	-	-	-	164.8	18.9	18	72
15	0.5	-	-	-	307.5	75.6	36	50
16 (Halad-9)	-	-	-	-	267.7	835.2	314	587

*An error of 10% is applied to viscosity data with no duplicate tests which is consistent with standard deviation values obtained from repeat measurements.

Table 5.5 Rheology of various cement slurries at 40°C

For a visual representation, data for both CMHEC as PEC and for CMHEC as raw material were plotted on a graph with respect to the percent of CMHEC in the system. This is shown in Figure 5.9.

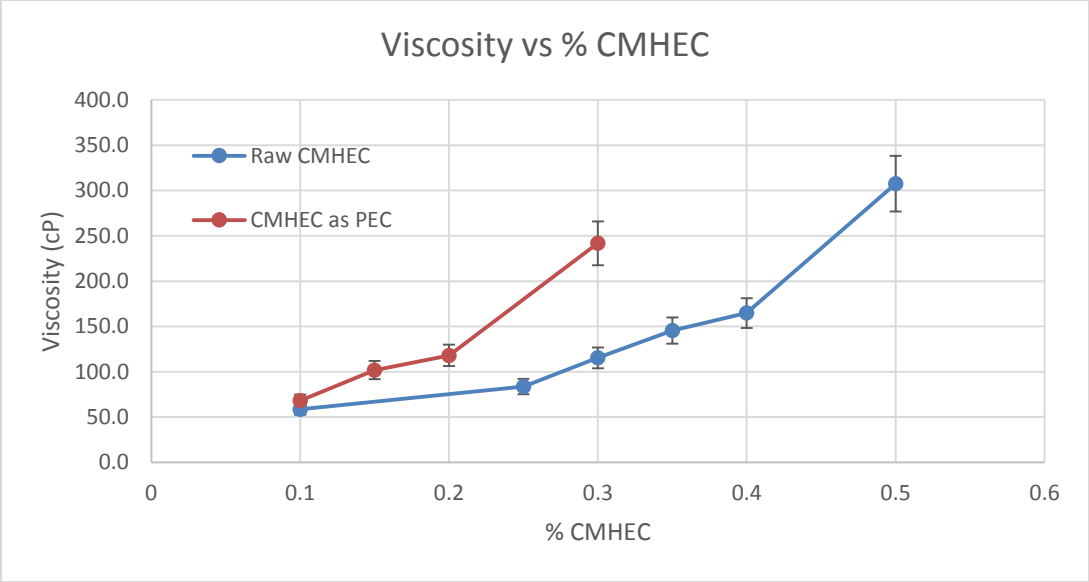


Figure 5.9 Plastic viscosity vs % CMHEC for PEC and raw material cases

At first glance there appears to be a significant disadvantage of the PEC system to that of raw CMHEC. The cement slurries with PECs are much higher in viscosity at a given concentration, with respect to % CMHEC, than the raw material. This is not a fair comparison, however, when consideration of the slurries' ability to control fluid loss is taken into account. When plotted against fluid loss control, the PEC's PV is below the raw material's result across the entire range from 0 to the API limit of 100mL/30min. This is shown visually in Figure 5.10.

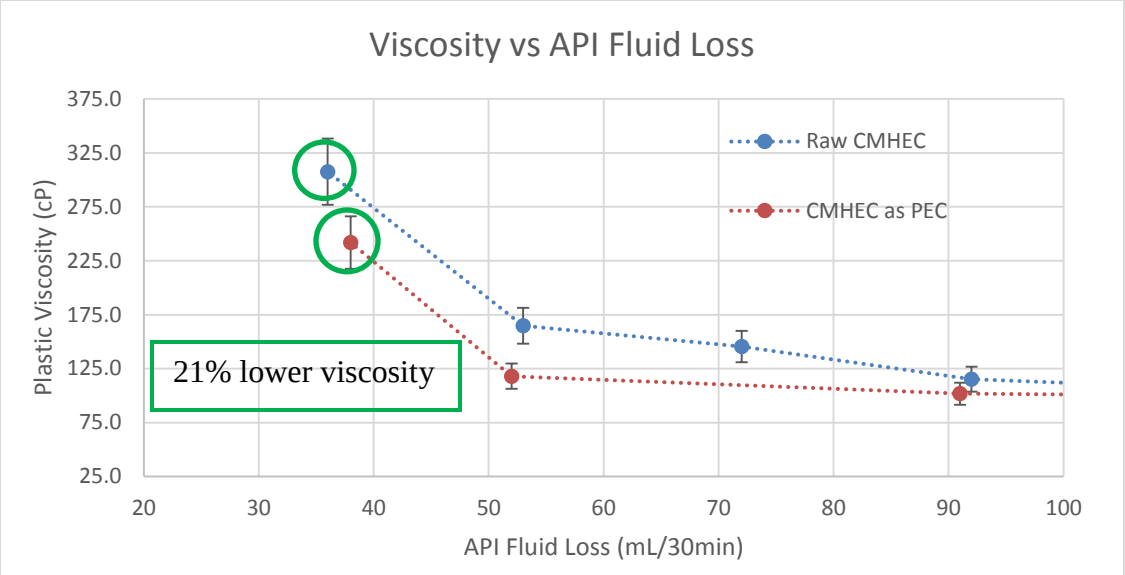


Figure 5.10 Plastic viscosity vs API fluid loss for CMHEC as PEC and raw material

Perhaps the most significant difference is seen when comparing the best recorded fluid loss value of each system. Even though the PEC achieves approximately the same fluid loss control as the raw material, its viscosity is approximately 20% lower. This means that the PEC provides nearly the same fluid loss control while being easier to pump than the baseline case of CMHEC as raw material.

To provide another point of evaluation, the PEC nanoparticle system was compared against the commercially available FLA, Halad®-9. Using the manufacturer's recommendations, 1.0% of the material was used with a small amount (0.1%) of HR-5 retarder for a sum of 1.1%bwoc total additives. This is comparable to the case of 0.3% CMHEC as PEC that also has 1.1%bwoc total additives (See Table 5.6).

FLA	FLA (mL/30min)	PV (cP)	YP (dyne/cm^2)	10s Gel (dyne/cm^2)	10m Gel (dyne/cm^2)
PEC	38	242	46	28	88
Halad-9	24	268	835	314	587

Table 5.6 Summary of important values for PEC and Halad-9 slurries

Although both systems are comparable with respect to fluid loss control, when it comes to rheology, the PEC excels in every regard. At just 242cP, the PEC's viscosity was approximately 10% lower than the commercial product. Furthermore, Halad-9, with a YP of over 835 dyne/cm^2 (or 84 Pa), is much more likely to result in a fractured formation during pumping than the PEC system due to the extra force needed to initiate flow. Obviously, in real life situations, dispersants would need to be added to lower the YP of the commercial slurry. However, this means purchasing more expensive additives. On the other hand, the PEC system is within a much more normal YP range without the need of extra additives.

With respect to gel strength, the commercial slurry gelled too fast and would therefore be prone to bridging and fluid communication. For the PEC system, on the other hand, the 10 minute gel strength was a reasonable 88 dyne/cm^2 (8.8 Pa) that is within the recommended criteria for a stable slurry (Baret et al., 2002). It must still be remembered that the gel strengths reported here are not the same as results from API's SGS test from which the recommended criteria were derived. The final determination on slurry stability will come from the results of the free fluid test.

Again, we see the possible capabilities of the PEC nanoparticle system. It has the ability to produce a slurry with acceptable rheology while continuing to meet the all-

important fluid loss control requirement. This adds further credibility to the abilities of PECs as ideal cementing additives.

To demonstrate the ability of the PEC to improve slurry viscosity by entrapping FLAs, compare Test #7 to Test #8 from Table 5.5. Both of these tests were performed with the same amount of reagents. Test #7, however, included CMHEC entrapped in the PEC whereas Test #8 did not. Notice that by entrapping CMHEC, the PV of the slurry decreases from 149cP to 118cP. This satisfies another criterion of this thesis, that by entrapping the FLA in a PEC, the viscosity can be reduced.

Rheological data for the 65°C case is summarized in Table 5.7.

Test #	% CMHEC	% PEI	% PAA	CHMEC in PEC?	PV* (cP)	YP ($dyne/cm^2$)	10s Gel ($dyne/cm^2$)	10m Gel ($dyne/cm^2$)
16	0.3	0.54	0.27	X	263.3	323.6	285	540
17	0.3	-	-	-	57.0	23.1	17	88
18	0.3	0.36	0.18	X	205.1	185.2	114	228
19	0.4	0.54	0.27	X	272.1	405.8	262	509
20	0.4	-	-	-	93.7	16.0	17	94

*An error of 10% is applied to viscosity data with no duplicate tests which is consistent with standard deviation values obtained from repeat measurements.

Table 5.7 Rheology of various cement slurries at 65°C

This data shows a notable increase in PV and an even more pronounced increases in YP, 10 second gel strength, and 10 minute gel strength tests of the PEC system at 65°C as compared to 40°C (Table 5.5). This rheology is definitely unfavorable and does not stand up against the raw material alone at the same concentrations (Tests #17 and #18 of Table 5.7). This is possibly due to the dissociation of PECs resulting in higher concentrations of free PEI in the system, which is known to cause an increase in slurry

viscosity (Dugonjić-Bilić et al., 2011). This is further supported by comparing Test #16 and Test #19, which contained equivalent amounts of PEI but different amounts of CMHEC. This data suggests that PEI dominates the viscosity of the slurry. The slight increase in PV from test #16 to #19 can be simply attributed to the additional CMHEC that is also known to be a viscosity enhancer.

Although the rheology at 65°C is not favorable, the fact that the PEC appears to dissociate at higher temperatures may actually be of value. With this knowledge, it seems feasible that one could create a PEC slurry system with a temperature triggered release of a certain substrate. For instance, a system could be devised to automatically deliver the right amount of retarder to a slurry based on the reservoir's temperature. A cool well would have less dissociation of nanoparticles and therefore release fewer retarding agents to the slurry. Meanwhile, a hot well would cause the PEC to dissociate more rapidly allowing for more retardation of the system. In theory, both wells could have the same curing time while having the same amount of PEC in the system. This could take some of the guess work out of finding the optimum concentrations of additives.

5.6 Free Fluid

The free fluid test at 40°C produced the following data, presented in Table 5.8.

Slurry	Free Fluid (%)
H-Cement	1.0
0.3% CMHEC	0.1
0.3% CMHEC as PEC	0.0

Table 5.8 Free fluid test data

As described earlier, any free fluid is an indication of a poor cement slurry. As expected (Roshan et al., 2010), slurries that contained CMHEC resulted in a significant reduction in free fluid. Furthermore, the PEC system with no free fluid showed an improvement over the raw material case. Most importantly, however, the PEC system satisfied the criteria of <0.5% free fluid to be considered a stable slurry. This data provides promise for the use of PECs as feasible cement additives.

5.7 Density

As expected, there were no significant concerns with regard to density. All slurries were within a normal range and produced values very close to that of H-Class cement. The values are listed in Table 5.9 below.

Slurry	Density (ppg) ±0.05
H-Cement	16.45
0.3% CMHEC	16.40
0.3% CMHEC as PEC	16.40

Table 5.9 Density test data

It is worthwhile to mention that the PEC system has not been tested with other density altering agents such as bentonite, barite, or hematite. Normally, these weighting additives would be mixed in the slurry to obtain the precise density required for the well

in question. However, it is not expected that these additives would have any significant effects on the functionality of the PECs.

5.8 Thickening Time

Thickening time results for 40°C temperatures are given in Table 5.10 and are represented graphically in Figure 5.11.

Time (hr)	**0.0**	**0.5**	**2.0**	**2.5**	**3.0**	**3.5**	**4.0**	**4.25**	**4.5**	**4.75**	**5.0**
Sample	Thickening Time (±2 Bc)										
H-Class Cement	8	12	14	15	18	24	31	36	40	46	53
0.3% CMHEC	6	5	6	6	6	6	6	6	6	6	7
PEC	10	11	13	13	13	14	14	14	14	14	14

Table 5.10 Thickening time test data

Not surprisingly, the slurries that contained CMHEC and/or PAA demonstrated much higher retarding effects than H-Class cement alone. This was expected as both components, by virtue of their carboxyl groups, are known to be effective retarders for cement. While a degree of retardation can be beneficial, especially given high reservoir temperatures, excessive retardation significantly increase the “waiting on cement” time at a well site and may lead to slurry instability.

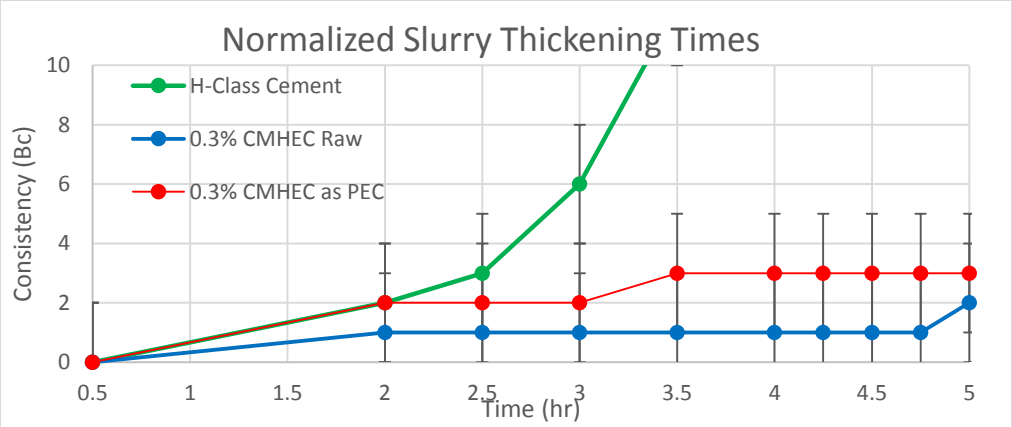


Figure 5.11 Normalized slurry thickening times

For 0.3% CMHEC as raw material the slurry showed very little increase in consistency even after 5 hours of conditioning. On the other hand, the trend of the PEC system resembles that of H-Class cement for the first 2 hours of testing before tapering off to a nearly level value resembling that of the raw material after approximately 3.5 hours. This is shown in Figure 5.11. Note that in this figure the consistency is normalized to zero at a conditioning time of 0.5 hours, which is the typical amount of time required for the slurry to reach temperature equilibrium.

The observed trend indicates that at least some of the polymers are entrapped in a nanoparticle up to approximately 2 hours. After this time, the PECs appear to degrade slowly up until approximately 3.5 hours. This results in a release of more retarding agents to the system, specifically CMHEC and PAA, leading to a more retarded system after approximately 3.5 hours than was observed initially. Although this data alone is hardly conclusive, it does add further credence to the possibility of applying a delayed release mechanism to control and alter the rheological properties of a cement slurry after placement.

CHAPTER VI

SUMMARY AND CONCLUSIONS

6.1 Summary

Oil well cementing is a complex process involving the interplay of numerous factors including rheology, density, fluid loss control, setting time, sedimentation, and gel strength development, to name a few. Polymers intended to provide solutions to these problems, however, often create unwanted side effects. For instance, additives that decrease the slurry viscosity to improve pumping may inadvertently lead to a mixture prone to undergo sedimentation and free water development. Alternatively, a polymer meant to control fluid loss and sedimentation may create a slurry that is too viscous and that cannot be pumped. Data on well barrier failures indicate that the complexities of oil well cementing have not been entirely solved. The industry is in need of improved cement systems to prevent the unwanted fluid communication and thereby reduce environmental impact and improve well performance.

PECs have proven to be useful in many industries for targeted and delayed release of substrates to prevent the unwanted side effects of competing reactions. Although this technology has found applications in oil recovery, very little work has been done to apply these ideas to oil well cementing. The purpose of this thesis was to provide a proof-of-concept study on the application of a simple PEC system to prevent fluid loss while producing a slurry with ideal rheological parameters.

This work demonstrated that a nanoparticle system comprised of CMHEC, PEI, and PAA could be added to a cement slurry to achieve a fluid loss of only 38mL/30min at 40°C with only 0.3%bwoc CMHEC as a PEC. This is over twice as effective as CMHEC alone and is comparable to a commercial product using the same total mass of additives. Furthermore, this PEC produced plastic viscosities across the entire acceptable range that were lower than control samples achieving the same fluid loss. These particles also met all API requirements for the tests in which they were subjected.

6.2 Conclusion

Based on the knowledge gained in this investigation, the following conclusions can be made:

1. PEC nanoparticles can be formed using common polymers already used in the oil well cementing industry, specifically CMHEC, PEI, and PAA.
2. Such PEC systems can provide exceptional fluid loss control at 40°C. At just 0.3% CMHEC as a PEC, a fluid loss of only 38mL/30 min. was obtained. By adjusting the design, it is reasonable to expect that a nanoparticle system could be modified to work at higher temperatures as well.
3. In addition to fluid loss control, the nanoparticle slurry system can maintain reasonable viscosity, stability, density, and gel strength development as demonstrated by the fact that all values remained within API specifications (where applicable).
4. By entrapping FLAs in a PEC, the viscosity of the system can be reduced.

5. The PEC system can be triggered to dissociate at high temperatures. This supports the idea of applying a delayed release mechanism to control the physical properties of a cement after initial placement. This functionality may allow a slurry to delay viscosity buildup until the cement is placed, at which time the viscosity and gel strength could increase rapidly to prevent fluid loss and settling.

Despite the success of the PEC system discussed in this thesis, more work must be done to produce a design that can be practically applied to the field. Such future considerations may involve developing nanoparticles that can control fluid loss at higher temperatures or utilizing different polymers, such as superplasticizers, to create a more fluid yet stable slurry. The idea of a delayed release may also be further exploited. For instance, a PEC may be engineered with the aim of delivering only the amount of retarder needed to appropriately treat the cement while preventing over-retardation. This would take some of the guess work out of slurry design and could improve the "waiting on cement" time and therefore improve efficiency.

In conclusion, the stated goals of this thesis were satisfied and the application of PECs to oil well cementing has thus far proven its utility.

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